

ATS-16506

Infrared Spectra of Molecules and Materials
of Astrophysical Interest

Grant NGL-41-002-003
Quarterly Progress Report
Report Number 25
September 1973

Office of Grants and Research Contracts
Office of Space Science and Applications
National Aeronautics and Space Administration
Washington, D. C. 20546

(Prepared under Grant NGL-41-002-003 by the
University of South Carolina, Columbia, South Carolina 29208)

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Period Covered: 15 June 1973 to 15 September 1973

(NASA-CR-139445) INFRARED SPECTRA OF
MOLECULES AND MATERIALS OF ASTROPHYSICAL
INTEREST Quarterly Progress Report, 15
Jun. - 15 Sep. 1973 (South Carolina
Univ.) 74 p

N74-75210

00/99 Unclassified
16506

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SPRINGFIELD, VA. 22161

SUMMARY OF PROGRESS

Gerard P. Kuiper¹ has pointed out that the Jovian atmospheres are expected to contain H_2 , He, N_2 , H_2O , NH_3 , CH_4 , Ar and possibly SiH_4 . He has also listed a number of other gases that should be considered because they are composed of fairly abundant atomic species and have boiling points below $120^\circ C$ [see Table 8, pg. 349-350 of reference (1)]. He has also pointed out that until more is known about the atmospheres of the planets, it is useful to keep a fairly large number of possible constituents in mind in planning further spectroscopic work.

We have been studying the vibrational spectra from 4000 to 33 cm^{-1} of several molecules which may be present in the atmosphere of the Jovian planets. These studies have been made to provide vibrational frequencies which can be used to: (1) determine the composition of the cloud covers of several of the planets; (2) provide structural information under favorable circumstances; (3) provide necessary data from which accurate thermodynamic data can be calculated; and (4) furnish information as to the nature of the potential energy function of the molecules and forces acting within them.

Some of the molecules which we have studied can be produced photochemically from methane, ammonia, and hydrogen sulfide which are thought to be constituents of the planets with reducing atmospheres. Some of the compounds will polymerize under ultraviolet radiation and drop out of the atmospheres. However, planets with a hot base, like that of Jupiter, may rebuild molecules destroyed photochemically. Therefore, we have used these criteria in selecting the compounds which we have studied. In our initial work on the vibrational spectra of molecules of astrophysical interest, we studied hydrazine,² methylamine³ as well as several substituted hydrazines.⁴⁻⁸ However, there are several other small molecules which contain carbon, hydrogen and nitrogen which also should be possible constituents of the reducing

atmospheres and we have been pursuing studies on several cyanide containing molecules.^{9,10} In the last progress report, we reported our investigation of the microwave and low frequency vibrational spectra of isopropylcyanide, $(\text{CH}_3)_2\text{CHCN}$. As a continuation of our work on these cyanide containing compounds, we have investigated the vibrational and rotational spectra of dimethylcyanophosphine.

There have been many microwave studies of molecules containing the CN group, especially the group IVA and VA nitriles, in order to determine the effect of the strong electron withdrawing group CN on the molecular structure.¹¹⁻³² In addition, there is the possibility of bonding through the nitrogen of the CN group to form the isocyanide compounds.^{11,33} Recently, in this laboratory we completed studies of isopropylcyanide, $(\text{CH}_3)_2\text{CHCN}$,¹⁰ and dimethylcyanamide, $(\text{CH}_3)_2\text{NCN}$.⁹ In the latter work, Li and Durig found evidence of significant electron delocalization on the apex nitrogen. As an extension of this work, we have investigated the microwave spectrum of $(\text{CH}_3)_2\text{PCN}$ for the purposes of trying to determine if there is any delocalization of the electron pair on phosphorus.

A vibrational study of $(\text{CH}_3)_2\text{PCN}$ was reported by Gobeau et al.³⁴ but their data was not complete. Therefore, we have investigated the far infrared, Raman, and infrared spectrum of this compound. The results of our studies of the rotational and vibrational spectra of this molecule can be summarized by the abstract of the paper which resulted from this work:

Abstract: The microwave spectrum of dimethylcyanophosphine has been recorded from 26.5 to 40.0 GHz. Only A-type transitions were observed. The R-branch assignments have been made for the ground state and three vibrationally excited states. It is shown that the heavy atom skeleton is nonplanar from the magnitude of the μ_c component of the dipole moment as well as from the value of $I_a + I_b - I_c$. The following structural parameters were obtained:

$r(\text{P-CN}) = 1.783\text{\AA}$, $\angle\text{CPC} = 101^\circ$, and $\angle\text{CPC}\equiv\text{N} = 99^\circ$ with reasonable assumptions made for the structural parameters of the dimethylphosphino moiety and the nitrile bond. These parameters are consistent with those previously reported for trimethylphosphine and tricyanophosphine. The dipole moment components were determined to be $\mu_a = 3.83 \pm 0.05\text{D}$ and $\mu_c = 1.5 \pm 0.1\text{D}$. A vibrational assignment has been made and from the low frequency vibrational data of the solid, a lower limit of 2.2 kcal/mole was obtained for the barrier to internal rotation of the methyl groups.

The results of this study have been submitted to the journal of Inorganic Chemistry for publication and the complete paper is given as Appendix I.

Another molecule which we studied these past three months and which satisfies the above criteria as a possible constituent of the Jovian atmosphere is 1,1-difluoroallene. There have been many studies of ethylene, C_2H_4 , but little structural information is available on allene, C_3H_4 . Allene does not have a permanent dipole but the 1,1-difluoro molecule is ideal for microwave studies. Therefore, we have completed an investigation of the low frequency vibrational and rotational spectra and determined the structural parameters. The results of this study are summarized by the abstract of the paper which resulted from this work:

Abstract: The microwave spectra of five isotopic species of 1,1-difluoroallene, H_2CCCF_2 , $\text{H}_2^{13}\text{CCCF}_2$, $\text{H}_2\text{C}^{13}\text{CCF}_2$, HDCCF_2 , and D_2CCCF_2 have been recorded from 12.4 to 40.0 GHz. A-type transitions were observed and R-branch assignments have been made for the ground and two vibrationally excited states. The following structural parameters have been determined: $r(\text{C}_1 = \text{C}_2) = 1.302 \pm 0.012\text{\AA}$; $r(\text{C}_2 = \text{C}_3) = 1.306 \pm 0.002\text{\AA}$; $r(\text{C}_1 - \text{F}) = 1.323 \pm 0.011\text{\AA}$; $r(\text{C}_3 - \text{H}) = 1.086 \pm 0.003\text{\AA}$; $\angle\text{HC}_3\text{H} = 117.8 \pm 0.2^\circ$; $\angle\text{C}_2\text{C}_3\text{H} = 121.1 \pm 0.1^\circ$; $\angle\text{FC}_1\text{F} = 110.2 \pm 1.0^\circ$;

$\angle \text{C}_2\text{C}_1\text{F} = 124.9 \pm 0.5^\circ$. The value of the dipole moment was obtained from Stark splittings to be $2.07 \pm 0.03\text{D}$. Coriolis coupling was observed between the two low frequency $\text{C} = \text{C} = \text{C}$ bending modes. The $\text{C} = \text{C} = \text{C}$ bending mode of B_1 symmetry (parallel to the CF_2 plane) has a frequency of 151 cm^{-1} whereas the one of B_2 symmetry has a frequency of 167 cm^{-1} . The dipole moment and structural values are compared to those of similar molecules.

The results of this study have been submitted to the Journal of Chemical Physics for publication and the complete paper is given as Appendix II.

The final piece of research which was completed these past three months included a study of the infrared and Raman spectrum of $\text{CH}_3\text{CCl}_2\text{F}$ and CH_3CHClF . There is little doubt that methane should be considered as a constituent of the Jovian atmospheres and ethane is a good candidate so we felt a study of some of the substituted ethanes would provide spectroscopically useful information. This was a short term project which was undertaken to provide some frequencies which can be used in our work on ethylamine and ethylphosphine. This study has been completed and the results submitted to the Journal of Raman Spectroscopy for publication. Our findings are given in Appendix III and the results are summarized by the abstract:

Abstract: The infrared spectra of gaseous and solid $\text{CH}_3\text{CCl}_2\text{F}$ and CH_3CHClF have been recorded from 140 to 4000 cm^{-1} . The corresponding Raman spectra of the liquids have also been recorded and depolarization values have been measured for the $\text{CH}_3\text{CCl}_2\text{F}$ molecule. Also the Raman spectrum of gaseous CH_3CHClF has been recorded. All spectra have been interpreted in detail and the 18 normal vibrations of both molecules have been characterized. The internal torsional mode for $\text{CH}_3\text{CCl}_2\text{F}$ was observed at 308 and 293 cm^{-1} in the spectra of the solid and gas, respectively. The threefold periodic barrier to internal rotation was calculated to be 6.08 kcal/mole for the solid

and 5.57 kcal/mole for the gas. The internal torsional mode for CH_3CHClF was observed at 261 cm^{-1} in the spectra of the solid and the barrier was calculated to be 4.38 kcal/mole. The barriers are compared in a series of chloro, fluoro, and bromo substituted ethane derivatives.

The work on methylchloroformate has not been quite finished but we hope to complete this study by the next reporting period. The vibrational study of dimethylamine has been completed but the interpretation of the low frequency torsional data is still uncertain. It certainly appears that the two methyl rotors are coupled by potential energy terms. Therefore, it will be necessary to treat these two rotors by a perturbation treatment which should provide quantitative values for the coupling terms V_{12} and V_{12}' .

We have now purchased the low temperature liquid helium cryostat which will be used for the molecular crystal work we proposed. In particular we shall study $(\text{CH}_3)_2\text{NH}$, N_2H_4 , P_2H_4 , and the N_2O_2 dimer.

FUTURE WORK

Work has been completed on dimethylamine and dimethylphosphine, both of which fit the criteria as possible constituents of the Jovian atmospheres. The interpretation of the low frequency data is not complete but we should be able to complete most of this work by the next reporting period. Work will be initiated on the study of $\text{C}_2\text{H}_5\text{NH}_2$ and $\text{C}_2\text{H}_5\text{PH}_2$. We are also initiating studies on biphosphine and we are continuing our work on methylchloroformate. We also plan to initiate vibrational studies of $\text{C}_2\text{H}_5\text{CN}$. This work is consistent with our work on $(\text{CH}_3)_2\text{NCN}$ and $(\text{CH}_3)_2\text{CHCN}$. We also expect to initiate studies on the vibrational spectra of azoethane, $(\text{C}_2\text{H}_5)_2\text{N}_2$, and its deuterium derivative.

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REFERENCES

1. G. P. Kuiper, Atmospheres of the Earth and Planets, University of Chicago, Chicago Press, Chicago, 1952.
2. J. R. Durig, S. F. Bush, and E. E. Mercer, J. Chem. Phys., 44, 4238 (1966).
3. J. R. Durig, S. F. Bush, and F. G. Baglin, J. Chem. Phys., 49, 2106 (1968).
4. J. R. Durig, W. C. Harris, and D. W. Wertz, J. Chem. Phys., 50, 1449 (1969).
5. J. R. Durig and W. C. Harris, J. Chem. Phys., 51, 4457 (1969).
6. J. R. Durig and W. C. Harris, J. Chem. Phys., 55, 1735 (1971).
7. J. R. Durig, R. W. MacNamee, L. B. Knight, and W. C. Harris, Inorg. Chem., 12, 804 (1973).
8. J. R. Durig, J. W. Thompson, and J. D. Witt, Inorg. Chem., 11, 2477 (1972).
9. Y. S. Li and J. R. Durig, J. Mol. Struct., 16, 433 (1973).
10. Y. S. Li and J. R. Durig, J. Mol. Struct., 17, 000 (1973).
11. M. Kessler, H. Ring, R. Trambarulo, and W. Gordy, Phys. Rev., 79, 54 (1950).
12. A. A. Westenberg and E. B. Wilson, Jr., J. Amer. Chem. Soc., 72, 199 (1951).
13. D. R. Lide, Jr., J. Chem. Phys., 22, 1577 (1954).
14. L. F. Thomas, E. I. Sherrard, and J. Sheridan, Trans. Faraday Soc., 51, 619 (1955).
15. W. Zeil, J. F. Pfrommer, Z. Electrochem., 61, 938 (1957).
16. J. G. Baker, D. R. Jenkins, C. N. Kenney, and T. M. Sugden, Trans. Faraday Soc., 53, 1397 (1957).
17. R. G. Lerner and B. P. Dailey, J. Chem. Phys., 26, 678 (1957).
18. T. Sparstad and E. Amble, J. Chem. Phys., 27, 317 (1957).
19. N. Müller and D. E. Pritchard, J. Amer. Chem. Soc., 80, 3483 (1950).
20. J. P. Friend and B. P. Dailey, J. Chem. Phys., 29, 577 (1958).
21. C. C. Costain and B. P. Stoicheff, J. Chem. Phys., 30, 777 (1959).
22. J. D. Graybeal, J. Chem. Phys., 32, 1258 (1960).
23. E. Hirota and Y. Morino, Bull. Chem. Soc. Japan, 33, 158 (1960).
24. E. Hirota and Y. Morino, Bull. Chem. Soc. Japan, 33, 705 (1960).
25. J. Sheridan and A. C. Turner, Proc. Chem. Soc., p.21 (1960).

26. J. D. Graybeal and D. W. Roe, J. Chem. Phys., 37, 2503 (1962).
27. L. J. Nugent, D. E. Mann, and D. R. Lide, Jr., J. Chem. Phys., 36, 965 (1962).
28. B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygard, J. Rastrup-Anderson, J. Chem. Phys., 37, 2027 (1962).
29. C. C. Costain and J. Yarwood, J. Chem. Phys., 45, 1961 (1966).
30. P. L. Lee, K. Cohn and R. H. Schwendeman, Inorg. Chem., 11, 1920 (1972).
31. L. Pierce, R. Nelson, and C. Thomas, J. Chem. Phys., 43, 3423 (1965).
32. P. L. Lee, K. Cohn, and R. H. Schwendeman, Inorg. Chem., 11, 1917 (1972).
33. L. F. Thomas, Heeks and J. Sheridan, Arch. Sci., 10, 180 (1957).
34. W. Koch, B. Blaich, and J. Goubeau, Rev. Chim. Minerale, 7, 1113 (1970).

MICROWAVE SPECTRUM, STRUCTURE, DIPOLE MOMENT AND LOW FREQUENCY
VIBRATIONS OF DIMETHYLCYANOPHOSPHINE.

ABSTRACT: The microwave spectrum of dimethylcyanophosphine has been recorded from 26.5 to 40.0 GHz. Only A-type transitions were observed. The R-branch assignments have been made for the ground state and three vibrationally excited states. It is shown that the heavy atom skeleton is non-planar from the magnitude of the μ_c component of the dipole moment as well as from the value of $I_a + I_b - I_c$. The following structural parameters were obtained: $r(\text{P-CN}) = 1.783\text{\AA}$, $\angle\text{CPC} = 101^\circ$, and $\angle\text{CPC}\equiv\text{N} = 99^\circ$, with reasonable assumptions made for the structural parameters of the dimethylphosphino moiety and the nitrile bond. These parameters are consistent with those previously reported for trimethylphosphine and thicyanophosphine. The dipole moment components were determined to be $\mu_a = 3.83 \pm 0.05\text{D}$ and $\mu_c = 1.5 \pm 0.1\text{D}$. A vibrational assignment has been made, and from the low frequency vibrational data of the solid a lower limit of 2.2 kcal/mole was obtained for the barrier to internal rotation of the methyl groups.

INTRODUCTION

There have been many microwave studies of molecules containing the $C\equiv N$ group, especially the Group IVA and VA nitriles, in order to determine the effect of the strong electron-withdrawing group CN on the molecular structure.¹⁻¹⁷ In addition, there is the possibility of bonding through the nitrogen of the CN group, to form the isocyanide compounds. Recently, in this laboratory, microwave and vibrational studies were completed on isopropylcyanide, $(CH_3)_2CHCN$,¹⁸ and dimethylcyanamide, $(CH_3)_2NCN$.¹⁹ In the latter work, Li and Durig¹⁹ found evidence of significant electron delocalization and a large contribution of sp^2 hybridization on the apex nitrogen. As an extension of this work, a microwave investigation of dimethylcyanophosphine has been undertaken.

A vibrational study of $(CH_3)_2PCN$ was conducted by Goubeau, et al.²⁰ but their assignment was incomplete. Therefore, Raman, infrared and far infrared data were obtained for the solid sample and a complete vibrational assignment is presented.

EXPERIMENTAL

The sample used in the present work was prepared by the method of Jones and Coskran²¹ and purified on a low temperature distillation column. Sample purity was confirmed by comparison of the ^{31}P NMR and mass spectral data with that previously reported.²¹

The microwave spectrum of $(CH_3)_2PCN$ was investigated in the frequency region 26.5 to 40.0 GHz using a Hewlett-Packard 8460A MRR spectrometer with a Stark modulation frequency of 33.33 KHz. The Stark cell was maintained at Dry Ice temperature for all measurements except those of relative intensity, which were performed at room temperature.

The infrared spectra were recorded from 4000 to 200 cm^{-1} with a Perkin-Elmer Model 621 spectrophotometer. The atmospheric water vapor was removed from the spectrophotometer housing by flushing with dry air. In the higher frequency region, the instrument was calibrated with standard gases.²² The lower wavenumber region was calibrated by using atmospheric water vapor and the frequencies reported by Hall and Dowling.²³ The spectrum of the solid was obtained by condensing the sample on a CsI plate maintained at -190° with boiling nitrogen.

The Raman spectrophotometer used was a Cary Model 82 equipped with a CRL Model 53A argon ion laser source. The spectrum of the room-temperature liquid was taken with the sample sealed in a capillary tube. The spectrum of the solid sample (-190°) was obtained by using a cell which was similar in design to a far infrared cell which was described earlier.²⁴ Depolarization measurements in the liquid phase were made by using the analyzer in the monochromator when making such measurements.

The far infrared spectrum was recorded from 33 to 590 cm^{-1} on a Beckman Model IR-11 spectrophotometer. The instrument was purged with dry nitrogen and calibrated with the frequencies reported for water vapor by Hall and Dowling.²³ The cell used for recording the spectrum of the solid at -190° has been described earlier.²⁴ The frequencies for all observed bands are expected to be accurate to $\pm 2\text{ cm}^{-1}$.

MICROWAVE SPECTRUM AND RESULTS

Preliminary spectral predictions for dimethylcyanophosphine were made using the reported structures of $\text{P}(\text{CN})_3$ ²⁵ and $(\text{CH}_3)_3\text{P}$.²⁶ These calculations indicated that the molecule was principally an A-type asymmetric rotor with an asymmetry parameter $K = -0.60$. A diagram of the molecule in the principal

axis system is given in Fig. 1. There was no apparent hyperfine structure observed due to the nitrogen quadrupole, and, therefore, no quadrupole coupling information was obtained from the present study.

The assignment was made mainly on the basis of the rigid rotor model fit. The Stark effects were also used to check some of the assigned transitions. The microwave spectrum and a computer plot of the spectrum generated from the fitted rotational constants are shown in Fig. 2. Around each ground state line, there are many weaker satellite lines which arise from molecules in excited vibrational states of low frequency modes.

The frequencies and assignments for the ground and three excited vibrational states and the differences between the observed and calculated frequencies are given in Table I. The observed rotational constants, moments of inertia and inertial defect terms for the ground and three excited vibrational states are given in Table II. The relative intensity of the three excited state satellites was measured with respect to the ground state line intensity for several transitions. The calculated energy level differences between the ground and excited vibrational state were: $\nu_{\alpha} = 252 \pm 20 \text{ cm}^{-1}$, $\nu_{\beta} = 201 \pm 10 \text{ cm}^{-1}$ and $\nu_{\gamma} = 178 \pm 15 \text{ cm}^{-1}$. The quoted error is derived from the standard deviation of the data.

A major problem of interest in the present study is the determination of the skeletal configuration of the $(\text{CH}_3)_2\text{PCN}$ molecule. From Table II, it can be clearly seen that the magnitude of $I_a + I_b - I_c$ is larger than that which would be observed from only the out-of-plane hydrogen atoms of the methyl groups. Thus, one can conclude that the heavy atom skeleton is nonplanar.

A complete structural determination is not possible from the present experimental information. In order to obtain some quantitative values for the nonplanarity and the $\text{P-C}(\equiv\text{N})$ bond distance, assumptions have been made in



dimethylphosphino parameters and the C≡N distance. An x-ray diffraction study of $P(CN)_3$ indicated a nonlinear P-C≡N angle of 172° .²³ This was attributed to requirements of crystal packing,²⁷ but recent work by Schwendeman, et al.¹⁶ determined the P-C≡N angle to be 171° in gaseous PF_2CN . The reason for this somewhat surprising angle is unclear, and for the purposes of this study, the P-C≡N angle was assumed to be 180° . A linear regression structure was calculated using the experimental rotational constants with the P-C(≡N) distance and the angle between the P-C≡N group and the CPC plane allowed to vary. Calculations were carried out for several values of the CPC angle in the dimethylphosphino group. The assumed parameters, results of the calculations, and the root sum square of the deviations between the observed and calculated moments of inertia, $[\sum \Delta I_g^2]^{1/2}$ $g = a, b, c$, are given in Table III.

DIPOLE MOMENT

The quadratic Stark effect of $(CH_3)_2PCN$ has been measured for the $|M| = 1$ component of the $5_{14} \leftarrow 4_{13}$ transition, the $|M| = 2$ component of the $6_{16} \leftarrow 5_{15}$ transition, and the $|M| = 1$ and $|M| = 2$ components of the $6_{25} \leftarrow 5_{24}$ transition. The $|M| = 2$ component of the $6_{16} \leftarrow 5_{15}$ transition showed a perturbation due to higher order terms in the Stark effect and was appropriately corrected. The electric field was calibrated using the $3 \leftarrow 2$, $|M| = 2$ transition of OCS with its dipole moment taken to be 0.7152 D.²⁸

VIBRATIONAL SPECTRUM AND RESULTS

The mid infrared, far infrared and Raman spectra of solid $(CH_3)_2PCN$ are shown in Figs. 3, 4, and 5. Since the heavy atom skeleton is nonplanar, the molecule belongs to symmetry group C_s and $15a'$ and $12a''$ modes are expected. The observed frequencies and their assignments are given in Table IV.

The assignment of the bands above 800 cm^{-1} is reasonably straightforward on the basis of relative intensities and expected frequencies. This leaves three skeletal stretches, five skeletal bends and two CH_3 torsions to be assigned. The C-P stretches are expected to be the highest frequency bands in this region, and the 673 cm^{-1} and 713 cm^{-1} bands are assigned to the symmetric, ν_{10} , and antisymmetric, ν_{24} , stretches of the methylcarbon-phosphorus bonds. The slightly lower band at 560 cm^{-1} is assigned as the C-P stretch, ν_{11} , involving the nitrile carbon. Of the five remaining skeletal modes, the three a' modes and the two a'' modes are expected to couple strongly and, hence, in the absence of any data for isotopically substituted molecules, their assignment is tentative. One possibility is to assign the 439 cm^{-1} band to the in-plane P-C \equiv N bend, ν_{12} , and the band at 238 cm^{-1} to the out-of-plane bend, ν_{25} . The band at 435 cm^{-1} in the Raman spectrum of the liquid was polarized, but no depolarization data were obtained for the 238 cm^{-1} band, which was not resolved in the spectrum of the liquid phase. The three C_3P deformations could then be assigned to the bands at 268 cm^{-1} , ν_{13} , 191 cm^{-1} , ν_{14} , and 158 cm^{-1} , ν_{27} . The shoulder at 204 cm^{-1} in the far infrared spectrum and the shoulder at 180 cm^{-1} in the Raman spectrum of the solid are tentatively assigned as the out-of-phase, ν_{26} , and in-phase ν_{15} , torsions, respectively. The weakness of the bands, as well as their relative frequencies is consistent with their being assigned as torsional motions.

DISCUSSION

The results of the structural calculation indicate that the angle between the CPC plane and the P-C \equiv N linkage is not very sensitive to the CPC angle in the $(\text{CH}_3)_2\text{P}$ moiety and the P-C(\equiv N) distance increases smoothly with an

increasing CPC angle. In Fig. 6 is shown a plot of the root sum square error versus the CPC angle. Thus, one obtains a CPC angle of 101° and a CPC(\equiv N) angle of 99° which are comparable with those found in $(\text{CH}_3)_3\text{P}$ ²⁶ and $(\text{CN})_3\text{P}$.²⁵

Since the nitrile group is more electronegative than the $(\text{CH}_3)_2\text{P}$ group, the dipole moment should be directed from the $(\text{CH}_3)_2\text{P}$ moiety to the negative center of the nitrile group. The dipole moment (3.83D) is less than that of $(\text{CH}_3)_2\text{NCN}$ (4.75D)¹⁹ which is to be expected if the lone pair of electrons in the phosphorous compound contribute less to the dipole moment than the lone pair in the nitrogen compound, as previous work suggests.^{17,29}

The calculated frequency of the excited vibrational state ν_α , $252 \pm 20 \text{ cm}^{-1}$, corresponds to ν_{13} , 268 cm^{-1} in the Raman spectrum of the solid. Also, ν_{13} is an a' mode and the value of $I_a + I_c - I_b$ for ν_α is not very different from that of the ground state. The assignment of ν_β , $201 \pm 10 \text{ cm}^{-1}$, and ν_γ , $178 \pm 15 \text{ cm}^{-1}$, is not as clear. Consistent with $I_a + I_c - I_b$ values for ν_β and ν_γ , they could be excited states of the out-of-phase and in-phase torsional motions, respectively. Or, on the other hand, they could be excited states of the two lowest skeletal deformations.

We have been interested in the barriers to internal rotation of methyl groups attached to phosphorous.³⁰⁻³³ Unfortunately, no barrier information was obtained from the microwave study of $(\text{CH}_3)_2\text{PCN}$. Barrier calculations were performed using the data from the vibrational studies and an F value of 5.23 cm^{-1} calculated using the proposed structure. One can calculate a barrier to internal rotation by assuming the interaction between the two tops is negligible. Using 204 cm^{-1} as a torsional frequency, one calculates a periodic barrier of 2.5 kcal/mole as a lower limit for the barrier in the solid sample. If one assumes the second torsion to correspond to the 180 cm^{-1} band, the internal rotation barrier is calculated to be 2.2 kcal/mole. These values are in qualitative



agreement with the barriers to internal rotation of methyl groups of 3.58 kcal/mole reported for $(\text{CH}_3)_3\text{P}$ ³² and 2.14 kcal/mole reported for $(\text{CH}_3)_2\text{PH}$.³⁴

ACKNOWLEDGMENT

The authors gratefully wish to acknowledge the financial support of this work by the National Aeronautics and Space Administration by Grant NGL-41-002-003.

REFERENCES

1. A. A. Westenberg and E. B. Wilson, Jr., *J. Amer. Chem. Soc.*, 72, 199 (1951).
2. L. F. Thomas, E. I. Sherrard, and J. Sheridan, *Trans. Faraday Soc.*, 51, 619 (1955).
3. J. G. Baker, D. R. Jenkins, C. N. Kenney, and T. M. Sygden, *Trans. Faraday Soc.*, 53, 1397 (1957).
4. R. G. Lerner and B. P. Dailey, *J. Chem. Phys.*, 26, 678 (1957).
5. J. P. Friend and B. P. Dailey, *J. Chem. Phys.*, 29, 577 (1958).
6. C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, 30, 777 (1959).
7. J. Sheridan and A. C. Turner, *Proc. Chem. Soc.*, p. 21 (1960).
8. J. D. Graybeal, *J. Chem. Phys.*, 32, 1258 (1960).
9. E. Hirota and Y. Morino, *Bull. Chem. Soc. Japan*, 33, 158 (1960).
10. E. Hirota and Y. Morino, *Bull. Chem. Soc. Japan*, 33, 705 (1960).
11. L. J. Nugent, D. E. Mann, and D. R. Lide, Jr., *J. Chem. Phys.*, 36, 965 (1962).
12. J. D. Graybeal and D. W. Roe, *J. Chem. Phys.*, 37, 2503 (1962).
13. B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Hygaard, J. Rastrup-Anderson, *J. Chem. Phys.*, 37, 2027 (1962).
14. L. Pierce, R. Nelson, and C. Thomas, *J. Chem. Phys.*, 43, 3423 (1965).
15. C. C. Costain and J. Yarwood, *J. Chem. Phys.*, 45, 1961 (1966).
16. P. L. Lee, K. Cohn, and R. H. Schwendeman, *Inorg. Chem.*, 11, 1917 (1972).
17. P. L. Lee, K. Cohn, and R. H. Schwendeman, *Inorg. Chem.*, 11, 1920 (1972).
18. Y. S. Li and J. R. Durig, *J. Mol. Struct.*, , 000 (1973).
19. Y. S. Li and J. R. Durig, *J. Mol. Struct.*, 16, 433 (1973).
20. W. Koch, B. Blaich, and J. Goubeau, *Rev. Chim. Minerale*, 7, 1113 (1970).
21. C. F. Jones and K. J. Coskran, *Inorg. Chem.*, 10, 1536 (1971).
22. IUPAC, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers", Butterworths, Washington, D. C., 1961.
23. R. T. Hall and J. M. Dowling, *J. Chem. Phys.*, 47, 2454 (1967); 52, 1116 (1970).
24. F. G. Baglin, S. F. Bush, and J. R. Durig, *J. Chem. Phys.*, 47, 2104 (1967).
25. K. Emerson and D. Britton, *Acta. Cryst.*, 17, 1134 (1964).



26. P. S. Bryan and R. L. Kuczkowski, J. Chem. Phys., 55, 3049 (1971).
27. F. A. Miller, S. G. Frankiss, and O. Sala, Spectrochim. Acta, 21, 775 (1963).
28. J. S. Muenter, J. Chem. Phys., 48, 4544 (1968).
29. J. R. Weaver and R. W. Parry, Inorg. Chem., 5, 718 (1966).
30. J. R. Durig, J. S. DiYorio, and D. W. Wertz, J. Mol. Spectrosc., 28, 444 (1968).
31. J. R. Durig and J. W. Clark, J. Chem. Phys., 50, 107 (1969).
32. J. R. Durig, S. M. Craven, and J. Bragin, J. Chem. Phys., 53, 38 (1970).
33. J. R. Durig and J. M. Casper, J. Phys. Chem., 75, 1956 (1971).
34. J. E. Saunders, Ph. D. Thesis, University of South Carolina, 1972.

Table I. Rotational Transitions of the Ground and Three Excited Vibrational States of Dimethylcyano-phosphine.

Transition	$v = 0$		$v_{\alpha} = 1$		$v_{\beta} = 1$		$v_{\gamma} = 1$	
	Obs.	Obs.-Calc.	Obs.	Obs.-Calc.	Obs.	Obs.-Calc.	Obs.	Obs.-Calc.
$5_{14} \leftarrow 4_{13}$	28748.66	0.29	28721.18	0.24			28743.56	0.22
$5_{24} \leftarrow 4_{23}$	27406.90	0.26	27379.67	-0.05	27437.90	0.09	27400.64	0.05
$6_{06} \leftarrow 5_{05}$	30675.86	0.12	30637.08	0.14	30730.31	0.18	30662.15	0.04
$6_{15} \leftarrow 5_{14}$	33995.45	0.03	33959.05	0.02	34045.63	0.28	33986.87	0.18
$6_{16} \leftarrow 5_{15}$	30447.41	0.13	30410.79	0.13	30495.27	0.13	30434.95	0.13
$6_{25} \leftarrow 5_{24}$	32676.67	-0.02	32643.15	0.00	32717.39	-0.07	32668.38	-0.04
$7_{07} \leftarrow 6_{06}$	35456.82	-0.03	35412.09	-0.11	35518.25	-0.02		
$7_{16} \leftarrow 6_{15}$	38973.23	-0.22	38927.34	-0.02	39041.32	-0.17	38960.16	-0.09
$7_{17} \leftarrow 6_{16}$	35336.25	0.01	35293.16	0.07	35393.05	-0.10	35321.32	0.09
$7_{26} \leftarrow 6_{25}$	37849.14	-0.19	37808.46	-0.29	37900.65	-0.19	37838.10	-0.40

60

Table II. Rotational Constants (MHz) and Moments of Inertia ($\text{amu}\cdot\text{\AA}^2$) of Dimethylcyanophosphine in the Ground and Excited Vibrational States.

	$v = 0$	$v_{\alpha} = 1$	$v_{\beta} = 1$	$v_{\gamma} = 1$
A	$5763.1 \pm .3$	$5750.6 \pm .2$	$5797.0 \pm .3$	$5759.2 \pm .4$
B	$3116.55 \pm .02$	$3114.57 \pm .01$	$3117.95 \pm .03$	$3116.78 \pm .03$
C	$2418.34 \pm .01$	$2415.29 \pm .01$	$2422.26 \pm .01$	$2417.18 \pm .01$
κ	-0.58250	-0.58067	-0.58771	-0.58134
I_a	87.693	87.883	87.179	87.751
I_b	162.159	162.262	162.087	162.147
I_c	208.976	209.241	208.638	209.077
$I_a + I_b - I_c$	40.875	40.904	40.628	40.820
$I_a + I_c - I_b$	134.51	134.86	133.73	134.68

Table III. Calculation of the Molecular Structure of Dimethylcyano-phosphine.

Assumed				Calculated			
r(P-C)	r(C-H)	r(C≡N)	∠HCH	∠CPC (degrees)	r(P-C) (Å)	σ ^a (degrees)	(Σ _g ΔI _g ²) ^{1/2} ^b Amu·Å ²
				97	1.779	104.3	4.08
				98	1.780	104.4	3.01
1.843 ^o Å	1.100 ^o Å	1.157 ^o Å	109.5°	99	1.781	104.4	1.94
				100	1.782	104.4	0.86
				101	1.783	104.4	0.20
				102	1.785	104.4	1.27
				103	1.786	104.4	2.33
				104	1.787	104.4	3.39
				105	1.789	104.3	4.44

^aAngle between CPC plane and the C≡N bond

^bΔI_g is the difference between the observed and calculated gth moment of inertia (g = a, b, c).

Table IV. Frequencies and Assignments for Dimethylcyanophosphine.

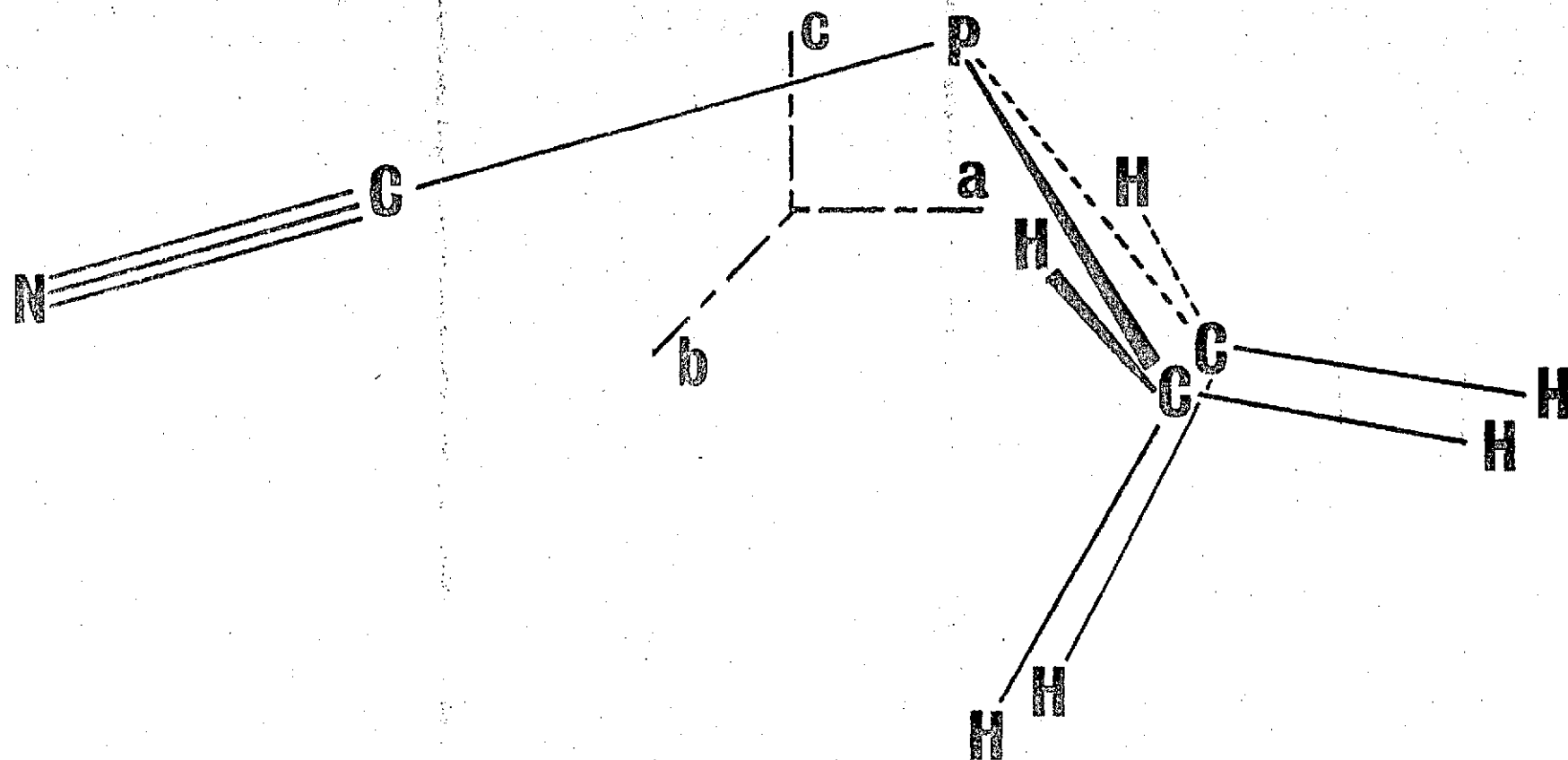
Raman (Solid)		Raman (Liquid)			Infrared (Solid)		Assignment
Frequency (cm^{-1})	Relative Intensity	Frequency (cm^{-1})	Relative Intensity	Polarization	Frequency (cm^{-1})	Relative Intensity	
2990	vs	2987	vs		2986	m	ν_1, ν_2 (a'), ν_{16}, ν_{17} (a'') CH_3 stretch
2917	vs	2915	vs		2920	w	ν_3 (a'), ν_{18} (a'') CH_3 stretch
2168	vvs	2170	vs		2170	w	ν_4 (a') $\text{C}\equiv\text{N}$ stretch
1433	s				1432	s	ν_{19} (a'') CH_3 deformation
1424	s				1421	s	ν_5 (a') CH_3 deformation
1412	m				1413	m	ν_{20} (a'') CH_3 deformation
1407	m	1403	w		1399	m	ν_6 (a') CH_3 deformation
1293	s	1288	w		1283	m	ν_7 (a') CH_3 deformation
1277	m				1274	m	ν_{21} (a'') CH_3 deformation
964	m	950	vw		963	s	ν_{22} (a'') CH_3 rock
915	w				913	s	ν_8 (a') CH_3 rock
886	m				884	s	ν_{23} (a'') CH_3 rock
835	w				840	s	ν_9 (a') CH_3 rock
713	vs	714	s	dp	713	s	ν_{24} (a'') C-P stretch
673	vs	668	vs	p	673	s	ν_{10} (a') C-P stretch
560	s	565	w	p	561	s	ν_{11} (a') P-CN stretch
439	m	435	w	p	441	w	ν_{12} (a') skeletal deformation
421	vw						two-phonon band

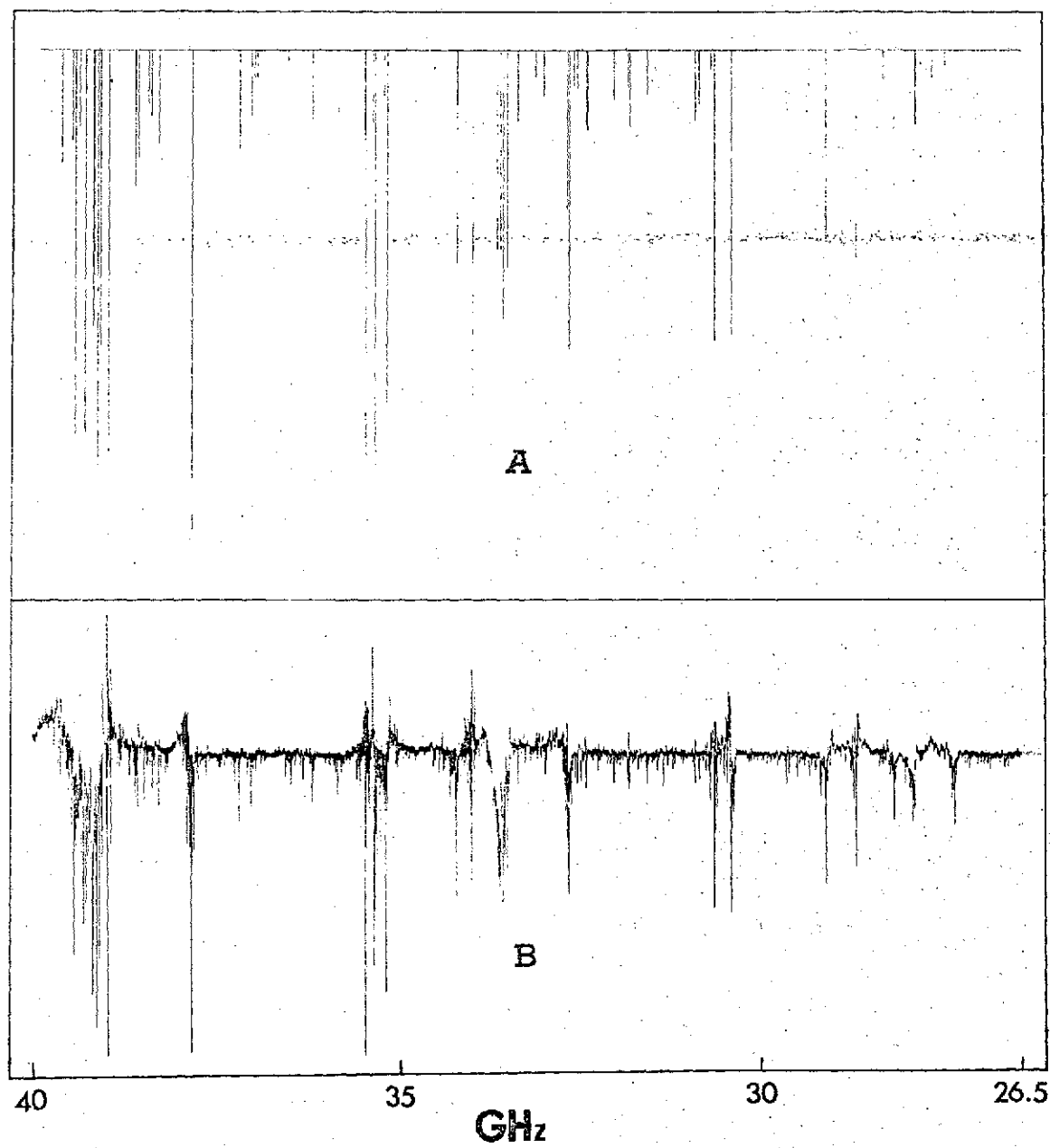
Table IV. Continued

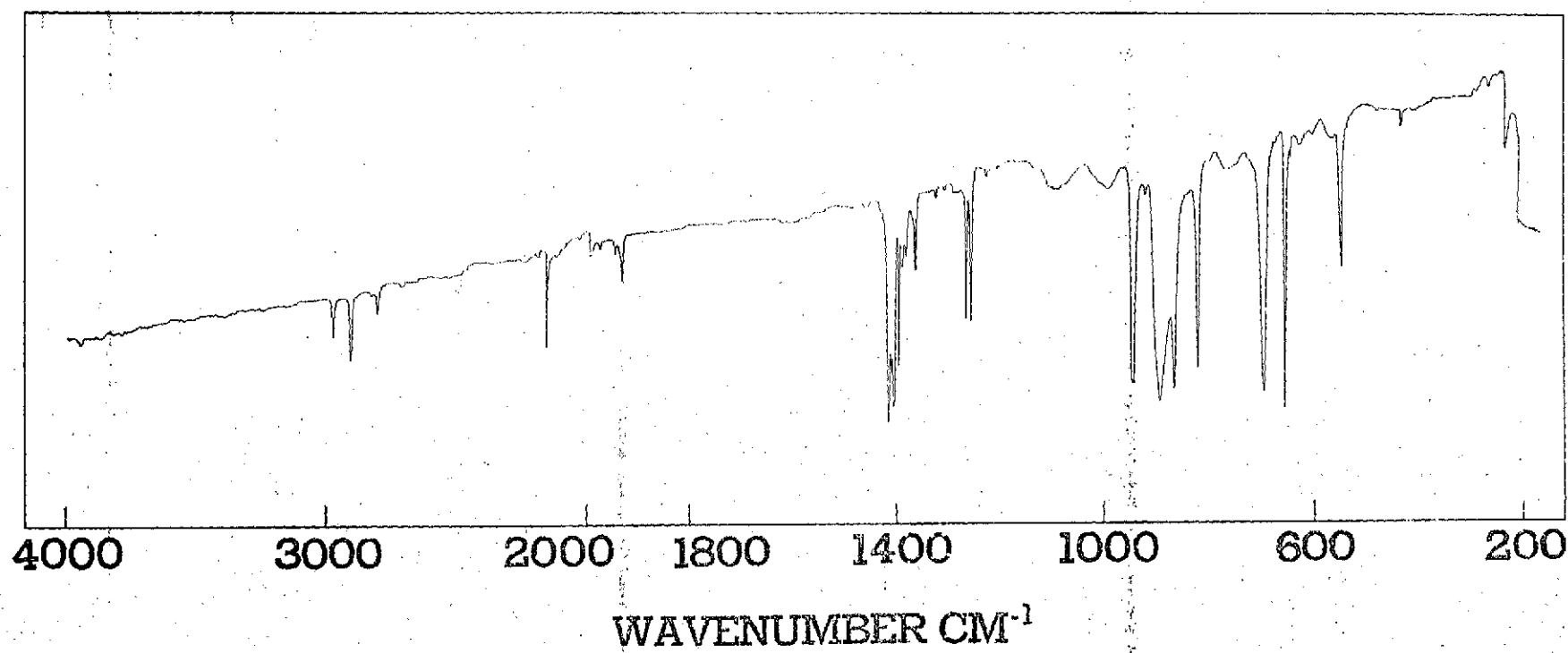
Raman (Solid)		Raman (Liquid)			Infrared (Solid)		Assignment
Frequency (cm^{-1})	Relative Intensity	Frequency (cm^{-1})	Relative Intensity	Polarization	Frequency (cm^{-1})	Relative Intensity	
268	m	268	w	p	276 (275)	w	ν_{13} (a') skeletal deformation
238	w				238 (236)	w	ν_{25} (a'') skeletal deformation
					206 (204)	vw	ν_{26} (a'') out-of-phase torsion (?)
191	s	190	s	p(?)	(184)	s	ν_{14} (a') skeletal deformation
180	vw						ν_{15} (a') in-phase torsion (?)
158	s	160	s	dp(?)	(162)	s	ν_{27} (a'') skeletal deformation
116	m						lattice modes
107	m						
90	s						
86	s						
60	m						
51	w						

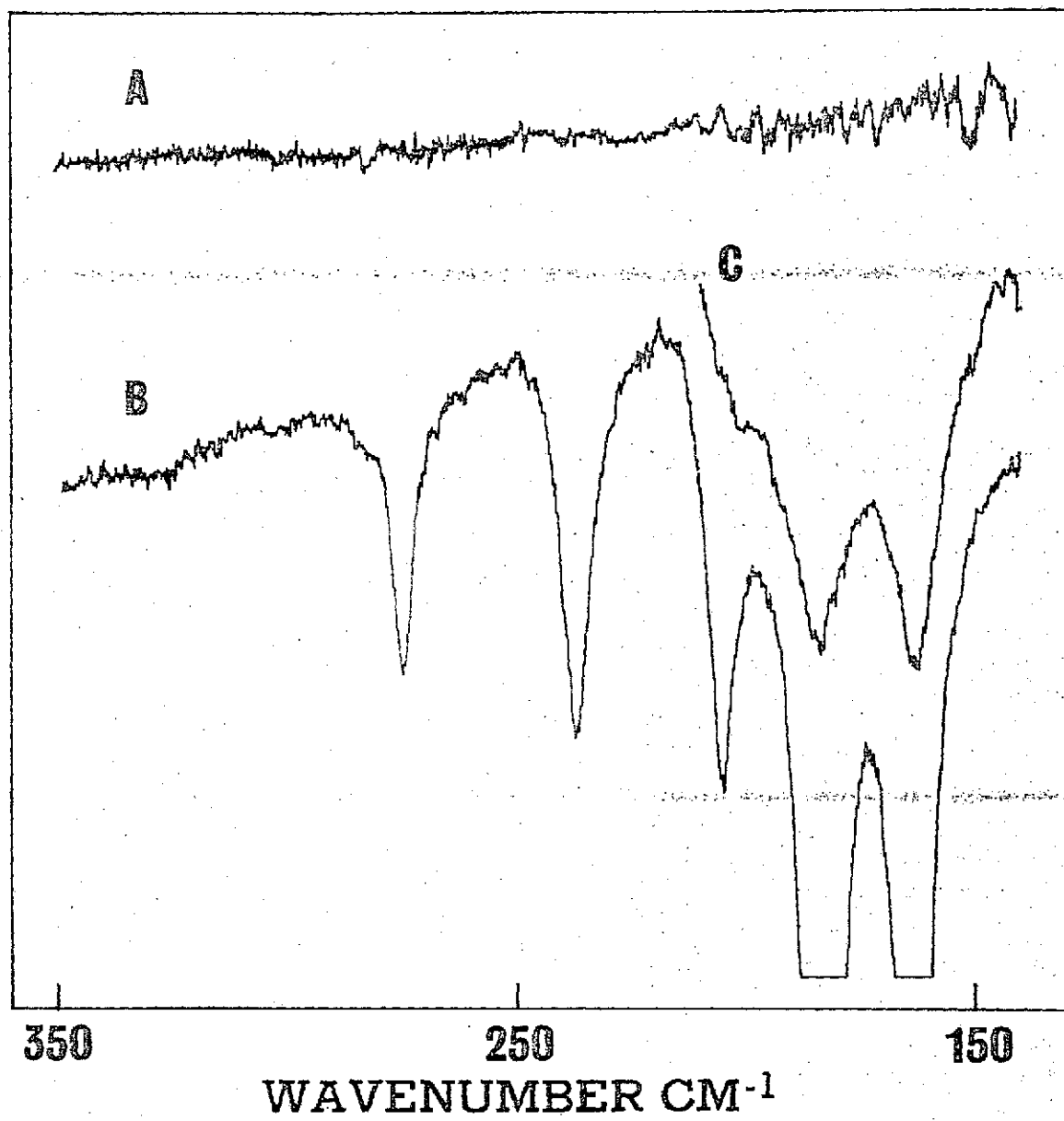
FIGURE CAPTIONS

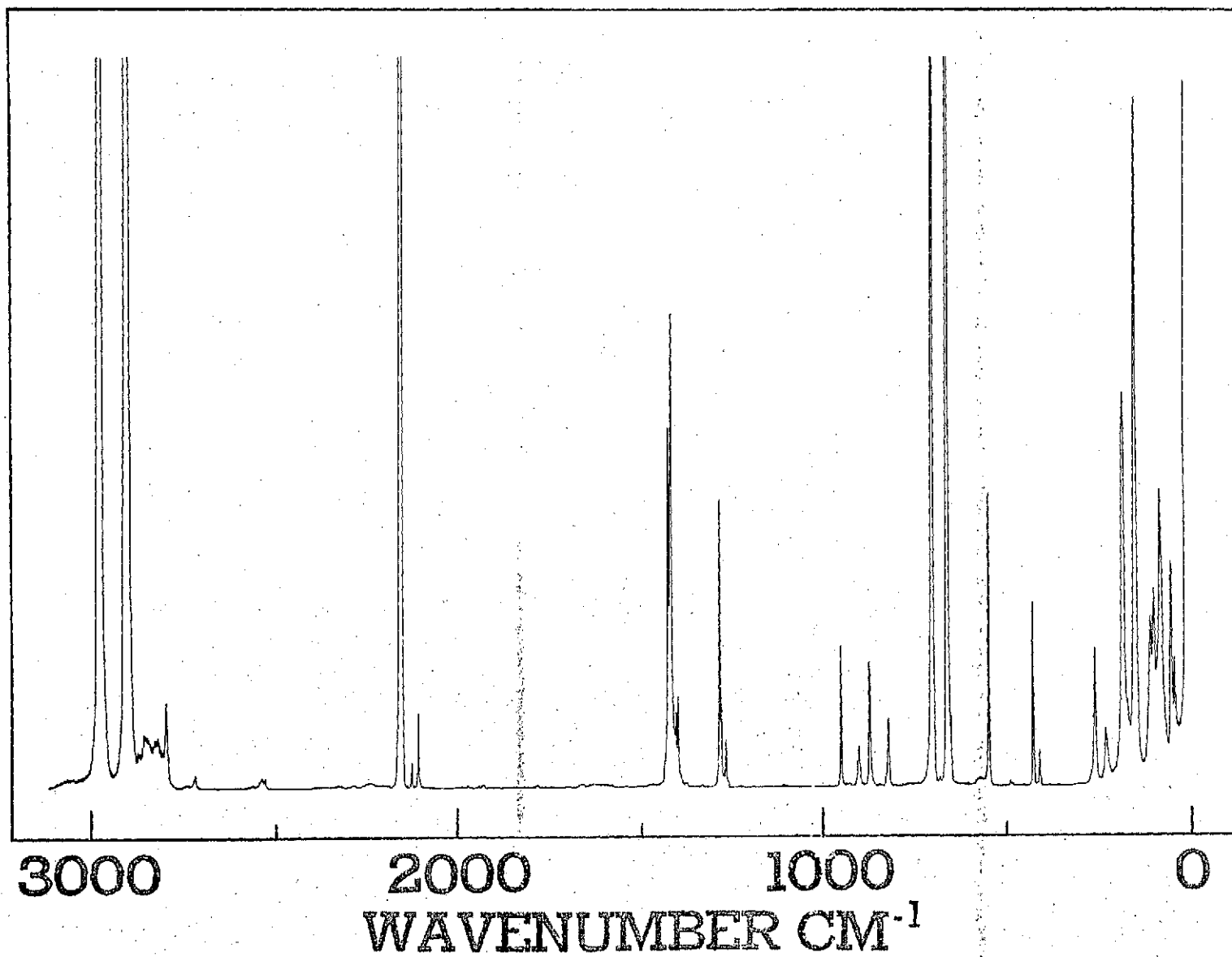
- Fig. 1. A projection of $(\text{CH}_3)_2\text{PCN}$ in its ac plane of symmetry.
- Fig. 2. A. A computer plot of the microwave spectrum of $(\text{CH}_3)_2\text{PCN}$ generated from the fitted rotational constants.
B. Microwave spectrum of $(\text{CH}_3)_2\text{PCN}$.
- Fig. 3. Infrared spectrum of $(\text{CH}_3)_2\text{PCN}$ at $\sim -190^\circ\text{C}$.
- Fig. 4. Far infrared spectrum of $(\text{CH}_3)_2\text{PCN}$ at $\sim -190^\circ\text{C}$.
A. Cell background
B. Annealed sample
C. Some sample evaporated
- Fig. 5. Raman spectrum of $(\text{CH}_3)_2\text{PCN}$ at $\sim -190^\circ\text{C}$.
- Fig. 6. Plot of the root sum square of the differences between the calculated and observed moments versus the CPC angle ϕ [in the $(\text{CH}_3)_2\text{P}$ group].

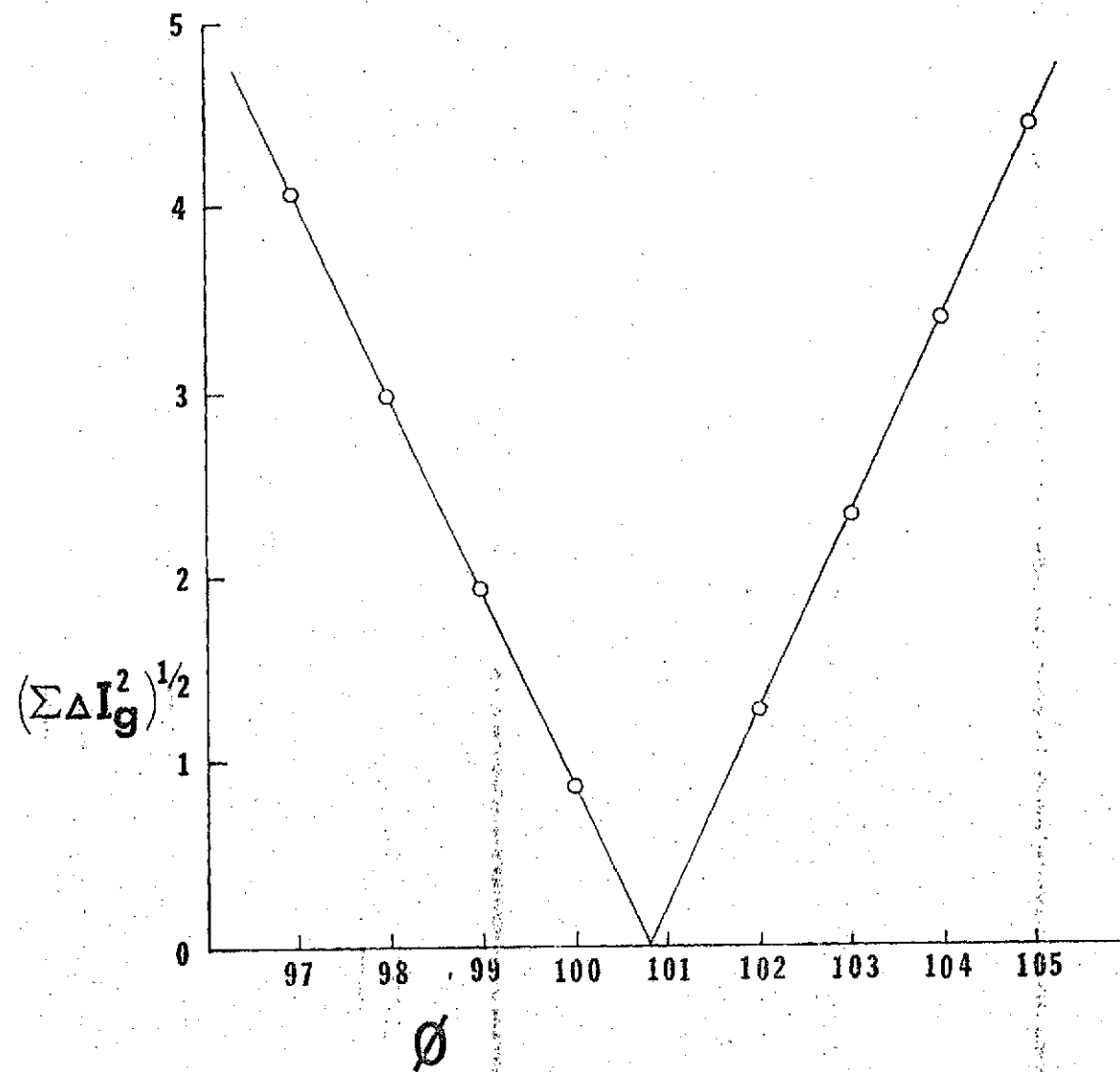












Microwave Spectrum, Structure, Dipole Moment and Coriolis Coupling
of 1,1-Difluoroallene

ABSTRACT: The microwave spectra of five isotopic species of 1,1-difluoroallene, H_2CCCF_2 , $\text{H}_2^{13}\text{CCCF}_2$, $\text{H}_2\text{C}^{13}\text{CCF}_2$, HDCCF_2 , and D_2CCCF_2 have been recorded from 12.4 to 40.0 GHz. A-type transitions were observed and R-branch assignments have been made for the ground and two vibrationally excited states. The following structural parameters have been determined: $r(\text{C}_1 = \text{C}_2) = 1.302 \pm 0.012 \text{ \AA}$; $r(\text{C}_2 = \text{C}_3) = 1.306 \pm 0.002 \text{ \AA}$; $r(\text{C}_1 - \text{F}) = 1.323 \pm 0.011 \text{ \AA}$; $r(\text{C}_3 - \text{H}) = 1.086 \pm 0.003 \text{ \AA}$; $\angle \text{HC}_3\text{H} = 117.8 \pm 0.2^\circ$; $\angle \text{C}_2\text{C}_3\text{H} = 121.1 \pm 0.1^\circ$; $\angle \text{FC}_1\text{F} = 110.2 \pm 1.0^\circ$; $\angle \text{C}_2\text{C}_1\text{F} = 124.9 \pm 0.5^\circ$. The value of the dipole moment was obtained from Stark splittings to be $2.07 \pm 0.03 \text{ D}$. Coriolis coupling was observed between the two low frequency $\text{C} = \text{C} = \text{C}$ bending modes. The $\text{C} = \text{C} = \text{C}$ bending mode of B_1 symmetry (parallel to the CF_2 plane) has a frequency of 151 cm^{-1} whereas the one of B_2 symmetry has a frequency of 167 cm^{-1} . The dipole moment and structural values are compared to those of similar molecules.

INTRODUCTION

An important objective of a theory of chemical shifts of diamagnetic molecules is the quantitative estimation of ^{13}C and ^1H NMR chemical shifts in organic molecules. This goal has often seemed remote due to problems associated with the gauge of the vector potential describing the magnetic field.¹ However, preliminary applications² of a recent gauge-invariant ab initio theory of magnetic shielding³ have given results for ^{13}C and ^1H chemical shifts which are in good agreement with experiment. To further document the performance of this method it is important to test it against experimental information for a variety of molecules. If sufficiently consistent success is obtained, this will allow some confidence to be acquired in its predictive power.

It is also important that the experimental systems chosen for the initial studies be inherently simple with respect to their structure and number of atoms, and yet exhibit the major types of substituent effect on shielding at carbon nuclei (e.g., inductive and mesomeric effects). A class of compounds which is particularly attractive from this point of view is the fluorocarbons. To this end we have recently determined the ^{13}C chemical shifts of the fluoroallenes, $\text{C}_3\text{F}_n\text{H}_{4-n}$.⁴ The measured ^{13}C shifts were compared to those predicted by SCF perturbation theory calculations employing a slightly extended Gaussian basis set of GIAO in an ab initio Molecular Orbital scheme.³ For these calculations, the geometry used was estimated from the standard geometrical model developed by Pople and Gordon.⁵ Although the level of agreement between the experimental data and the predicted results was good, it is essential to employ the best structural data possible in such calculations. With this goal in mind, we investigated the microwave spectrum of 1,1-difluoroallene and four of its isotopic species. The results of this study are reported herein.

EXPERIMENTAL

The sample of 1,1-difluoroallene- d_0 (H_2CCCF_2) was prepared by the following procedures. Dibromodifluoromethane (272 g), ethylene (8.4 g) and benzoyl peroxide (5 g) were placed in a bomb at $110^\circ C$ for 5 hours. The product, 1,3-dibromo-1,1-difluoropropane, was purified by distillation at $62^\circ C$ and 86 mm pressure to give 42 g (59% conversion of ethylene) of propane. The propane was then decomposed ($-2HBr$) with molten potassium hydroxide at $140^\circ C$. The product was swept into liquid nitrogen cooled traps on a standard high vacuum line with helium as the carrier gas. The crude 1,1-difluoroallene was then distilled on a low temperature fractionation column.⁶ The distillation yielded 3.2 g of 1,1-difluoroallene (24% conversion of propane). The purity of the 1,1-difluoroallene was checked by the infrared data reported by Blomquist and Longone.⁷ The 1,1-Difluoroallene- d_1 sample was prepared in 50% isotopic purity by using ethylene- d_1 in the above synthesis of 1,1-difluoroallene- d_0 . Ethylene- d_1 was prepared by dropping D_2O on to vinyl lithium in tetrahydrofuran. The gaseous product was swept into liquid nitrogen cooled traps on a high vacuum line. The crude ethylene- d_1 was then distilled on a low temperature fractionation column. The 1,1-difluoroallene- d_2 sample was synthesized by the use of ethylene- d_4 in the same synthetic route as given above for 1,1-difluoroallene- d_0 . Ethylene- d_4 was obtained by the method of Leitch and Morse.⁸ The isotopic purity of the 1,1-difluoroallene- d_2 obtained from this synthesis was determined from mass spectral data to be 93%. Both carbon-13 species were studied in their naturally occurring abundance.

The microwave spectra were investigated using a Hewlett-Packard Model 8460 A MRR spectrometer in the frequency regions 12.4 - 40GHz. The Stark cell was modulated with a square wave of 33.3 KHz in frequency. Frequency measurements were made with the cell being cooled with Dry Ice and the accuracy was better than 0.05 MHz.

SPECTRA

Because of the molecular symmetry, 1,1-difluoroallene is expected to have only one type of microwave transition. Based upon a preliminary structural estimate, 1,1-difluoroallene should have the principle a-axis directed along the CCC bond with the b-axis in the F_2C plane. The observed spectra were characteristic of an asymmetric rotor with a-type selection rules. Initial assignment was made from a careful Stark study and a rigid rotor model fit. Listed in Table I are the measured frequencies of the identified transitions along with the frequency difference from those calculated with the rotational constants listed in Table II. For the measured transitions, it is believed that the centrifugal distortion introduces little effect on the rotational constants; therefore no correction for this effect has been made. Spectra arising from the naturally abundant ^{13}C isotopic species, $H_2^{13}CCCF_2$ and $H_2C^{13}CCF_2$, were essentially identified from the intensity study at different temperatures.

In addition to the ground state lines, there are many other lines surrounding it. These lines are believed to be due to the rotational transitions of the molecules in the excited vibrational states. Measurements have been made on the two strongest satellites for H_2CCCF_2 , $HDCCF_2$ and D_2CCCF_2 . Given in Table III are the excited state transitions of these three isotopic species and it was found that the frequencies fit the rigid rotor approximation. The effective rotational constants and the moments of inertia for these vibrationally excited states are listed in Table IV. It will be shown in a later section that these data are useful for obtaining the Coriolis coupling information.

The carbon atom bonded directly to the fluorine atoms is rather close to the center of mass of the molecule. The resulting small shifts from the carbon-12 lines make it difficult to identify the rotational transitions of $H_2CC^{13}CF_2$, since there is a good possibility that they will be overlapped by the rather intense, excited vibrational state lines.

STRUCTURE

The experimental moments of inertia of H_2CCCF_2 , $\text{H}_2^{13}\text{CCCF}_2$, $\text{H}_2\text{C}^{13}\text{CCF}_2$ and HDCCCF_2 should give sufficient information for determining the coordinates of H, C_3 and C_2 atoms by using the isotopic substitution method.⁹ The substituted coordinates in the principal axis system of H_2CCCF_2 are, therefore, calculated and listed in Table V. After obtaining these coordinates, the next procedure was to determine the coordinates of C_1 , F_1 and F_2 atoms by use of the center of mass condition as well as the moments of inertia relations. Molecular symmetry makes only three independent coordinates required for locating the positions of these three atoms. Consequently, the available information is greater than the number of unknowns. The mean coordinates obtained are listed in Table V and the corresponding structure is given in Table VI. It is difficult to determine all the possible errors. From the uncertainty in the experimental moments of inertia, one would obtain the errors to be 0.002\AA , 0.003\AA , and 0.2° for the C_2C_3 , C_3H distances and $\text{H}_1\text{C}_3\text{H}_2$ angle, respectively. From both the uncertainty in the observed moments of inertia and the consistency of the coordinates obtained from different combinations of data the estimated errors for the C_1C_2 , C_1F distances and F_1CF_2 angle are found to be 0.012\AA , 0.011\AA and 1.0° , respectively.

Instead of obtaining the coordinates of the hydrogen atoms from the moments of inertia of H_2CCCF_2 together with those of HDCCCF_2 , one may also determine the coordinates with the experimental results of the H_2CCCF_2 and D_2CCCF_2 molecules. This set of data has led to the values of $a_{\text{H}} = 2.8463$ and $C_{\text{H}} = 0.9301\text{\AA}$ which are essentially identical with those obtained in the earlier calculation. The resulting structural parameters are found to be: $r(\text{CH}) = 1.086\text{\AA}$, $\angle\text{HCH} = 117.8^\circ$, $r(\text{C}_2\text{C}_3) = 1.306\text{\AA}$, $r(\text{C}_1\text{C}_2) = 1.304\text{\AA}$, $r(\text{C}_1\text{F}) = 1.322\text{\AA}$ and $\angle\text{FCF} = 110.3^\circ$.

which are in excellent agreement with the corresponding parameters given in Table VI obtained by the earlier method.

DIPOLE MOMENT

The electric dipole moment of 1,1-difluoroallene has been determined by measuring the following Stark components: $|M| = 0, 1, 2$ of the $3_{03} \leftarrow 2_{02}$ transition, $|M| = 1, 2$ of the $3_{12} \leftarrow 2_{11}$ transition and $|M| = 1$ of the $3_{13} \leftarrow 2_{12}$ transition. Each measured component was observed to have the quadratic Stark effect. The electric field was calibrated by using the $2 \leftarrow 1$ transition of OCS at 24325.92 MHz with its dipole moment taken as 0.71521 D.¹⁰ The data were analyzed by the method of Golden and Wilson.¹¹ Because of the molecular symmetry each measured component gives a value of the dipole moment. Listed in Table VII is the result of this Stark study and μ_a was found to have a value of 2.07 ± 0.03 D. The quoted uncertainty represents the standard deviation obtained from the different Stark measurements.

Coriolis Coupling

The H_2CCCF_2 and D_2CCCF_2 molecules have C_{2v} symmetry and in a recent vibrational study of 1,1-difluoroallene¹² we observed Raman lines in the gaseous state at 167 and 151 cm^{-1} with shoulders at 151 and 145 cm^{-1} for the samples of H_2CCCF_2 and D_2CCCF_2 , respectively. These two lines may be assigned to the two CCC bending motions (ν_{11} and ν_{15}) which belong to symmetry species B_1 and B_2 . However, there is ambiguity in the assignments of ν_{11} and ν_{15} as to which mode should have the higher frequency. $B_1 \times B_2$ has the same symmetry as the rotational angular momenta p_z and the first condition for strong perturbation is satisfied. Furthermore,

the two vibrational energy levels are sufficiently close to give some observable corrections to the rigid rotor energy levels. In the molecular system, z has the same direction as principle axis a . Consequently, ν_{11} will couple with ν_{15} when the rotation about the a -axis is excited.

If only the coupling between ν_{11} and ν_{15} is considered the change in the effective moment of inertia I_a from the ground state to the first excited state can be expressed by the approximate forms:¹⁴

$$I_a(\nu_{11} = 1) - I_a(\nu = 0) \sim (8k/\nu_{11})[\nu_{15}^2/(\nu_{15}^2 - \nu_{11}^2)] (\zeta_{11,15}^a)^2 \quad (1)$$

and

$$I_a(\nu_{15} = 1) - I_a(\nu = 0) \sim (8k/\nu_{15})[\nu_{11}^2/(\nu_{11}^2 - \nu_{15}^2)] (\zeta_{11,15}^a)^2 \quad (2)$$

where $k = h/8\pi^2c$, ν is the vibrational frequency, and $\zeta_{11,15}^a$ is the Coriolis coupling constant. It can be seen from Tables II and VI, that the $(0,1)$ state has a larger value of I_a than $\nu(0,0)$; therefore, one expects it to have a lower energy state than the $\nu(1,0)$ state. The opposite is true for the $\nu(0,1)$ state since I_a in the $\nu(0,1)$ state is smaller than that in the $\nu(0,0)$ state. By using the vibration frequencies and the moments of inertia along with the above expressions, one estimates the squares of the Coriolis coupling constants to be 0.11, 0.16 and 0.11, 0.15 for the H_2CCCF_2 and D_2CCCF_2 molecules, respectively.

The $HDCCCF_2$ molecule has C_s molecular symmetry and its corresponding bending motions belong to A' and A'' modes, respectively. The product of these two species has the same symmetry as the rotation about either the a -axis or b -axis. With the vibrational frequencies of 167 and 151cm^{-1} , one estimates by a similar process the value of $(\zeta_{11,15}^a)^2$ to be 0.13 and 0.18 for $HDCCCF_2$. From a comparison of the values of I_a 's at different states, it is also found that $\nu(0,1)$ is in a lower energy state than $\nu(1,0)$.

DISCUSSION

The dipole moment of 1,1-difluoroallene (2.07D) is rather large in comparison to the dipole moment (1.37D) of 1,1-difluoroethylene.¹⁵ Such a variation of dipole moment with number of carbons in the chain may be rationalized by the alternation effect as given by Pople and Gordon⁵, in their calculation of the dipole moments of a series of simple organic compounds.

The C=C bond distances of 1.306 and 1.302 Å obtained for 1,1-difluoroallene do not indicate any significant differences from the corresponding bond lengths in allene.^{16,17} The experimental uncertainties in the bond lengths also limit the significance of the difference in the two C=C bonds which might be caused by the fluorine substitution. The C-F bond distance (1.323 Å) is identical with that in H₂CCF₂¹⁸. Although the listed value of the FC₁F angle (110.2°) is larger (109.1°) than that in H₂CCF₂¹⁸, the experimental error again prevents any significance being placed on the difference. The structure of the methylene (CH₂) group in H₂CCF₂ is quite typical.¹⁷

In 1962, Bernstein¹⁹ showed a close relation between the averaged CH stretching frequency of a molecule and its CH bond length. In the absence of resonance, Duncan²⁰ has demonstrated the correlation between the separation of asymmetric and symmetric CH₂ stretching frequencies and the HCH angle in the =CH₂ group of a molecule. From the closeness of the CH₂ geometries of allene and 1,1-difluoroallene, one would, thus, expect little difference in their CH stretching frequencies.

It was concluded in the Coriolis coupling section that the v(0,1) state has a lower energy than the v(1,0) state. Both vibrational modes (B₁ and B₂) are antisymmetry with respect to the C₂ operation. For the same rotational transition, both satellites should have the same statistical weights. Our relative intensity measurement has indicated consistently for all three isotopic

species that the $v(0,1)$ state has a lower energy than the $v(1,0)$ state. This result is in complete agreement with that obtained from the vibration and rotation interaction study.

In an attempt to make an assignment to the bending motions, one has to assume a reasonable picture for the normal modes of vibration. If the molecule is excited to the $v_{11} = 1$ state in which the C=C=C bending occurs in the CF_2 plane, one expects a smaller value of $\Delta_c = I_a + I_b - I_c$ than the corresponding value in the ground state. On the other hand, the excitation of the bending motion¹⁵ perpendicular to the CF_2 plane will result in a larger value of Δ_c . By combining these data with that given in Tables II and VI, one predicts that the 151 cm^{-1} line $v(0,1)$ is the bending state parallel to the CF_2 plane and the 167 cm^{-1} line is the bending mode perpendicular to the CF_2 plane. Thus, we get $v_{11} = 151$, $v_{15} = 167\text{ cm}^{-1}$, and $v_{11} = 151$, $v_{15} = 145\text{ cm}^{-1}$ for H_2CCCF_2 and HD_2CCCF_2 , respectively.

The structural parameters employed in the chemical shift calculations for 1,1-difluoroallene were $r(C_1-C_2) = r(C_2-C_3) = 1.31\text{Å}$, $r(C_1-F) = 1.33\text{Å}$, $r(C_3-H) = 1.08\text{Å}$ and all angles were taken at 120.0° . The distances used for these calculations are comparable to those found in this study. However, there are significant differences between the angles employed in the calculations and those obtained in the microwave study. In particular, the $\angle FC_1F$ of $110.2^\circ \pm 1.0^\circ$ is considerably smaller than 120° and it is expected that such a difference could lead to significant changes in the predicted shielding constants.

It should be of interest to compare the dipole moments and the structures for a series of fluorine substituted allenes. Also, it appears that additional structure work on these molecules would be of interest in attempting to predict shielding constants. Therefore, further microwave work on some of these molecules is warranted and we hope to initiate such studies in the near future.

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ACKNOWLEDGMENT

P. D. Ellis and A. P. Zens are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society for partial support of this research. Also, the authors wish to acknowledge Mr. Alan D. Cardin for assistance in some of the synthetic work. J. R. Durig, Y. S. Li and C. C. Tong acknowledge the financial support given this work by the National Aeronautics and Space Administration by Grant number NGL-41-002-003.

REFERENCES

1. For a recent review see W. N. Lipscomb, *Adv. Magn. Resonance*, 2, 137 (1966).
2. R. Ditchfield, *Chem. Phys. Lett.*, 15, 203 (1972).
3. R. Ditchfield, *J. Chem Phys.*, 56, 5688 (1972)
4. A. P. Zens, P. D. Ellis, R. Ditchfield, submitted to *J. Amer. Chem. Soc.*
5. J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, 89, 4253 (1967)
6. J. Dobson and R. Schaeffer, *Inorg. Chem.*, 9, 2183 (1970).
7. A. T. Blomquist and D. L. Gongone, *J. Amer. Chem. Soc.*, 79, 4981 (1957)
8. L. C. Leitch and A. T. Morse, *Can. J. Chem.*, 30, 924 (1952).
9. J. Kruitchman, *Am. J. Phys.*, 21, 17 (1953).
10. J. S. Muentner, *J. Chem Phys.*, 48, 4544 (1968).
11. S. Golden and E. B. Wilson, Jr., *J. Chem Phys.*, 16, 669 (1948).
12. J. R. Durig, Y. S. Li, A. P. Zens, P. D. Ellis and J. D. Witt, to be submitted.
13. E. B. Wilson, Jr., *J. Chem Phys.*, 4, 313 (1936).
14. V. W. Lourie and D. T. Pence, *J. Mol. Spectrosc.*, 10, 155 (1963).
15. A. Roberts and W. F. Edge11, *J. Chem Phys.*, 17, 742 (1949).
16. A. Lemnningen, O. Bastiansen and M. Tretteberg, *Acta Chem. Scand.*, 13, 1699 (1959).
17. A. G. Maki and R. A. Toth, *J. Mol. Spectrosc.*, 17, 136 (1965).
18. V. W. Lourie and D. T. Pence, *J. Chem. Phys.*, 38, 2693 (1963).
19. H. J. Bernstein, *Spectrochim. Acta*, 18, 161 (1962).
20. J. L. Duncan, *Spectrochim. Acta*, 26A, 429 (1970).

Table I. Rotational Frequencies in MHz of 1,1-Difluoroallene and its Carbon 13 and Deuterated Isotopic Species in the Ground Vibrational State.

$J' \leftarrow J$	H_2CCCF_2		$\text{H}_2^{13}\text{CCCF}_2$		$\text{H}_2\text{C}^{13}\text{CCF}_2$		HDCCCF_2		D_2CCCF_2	
	$\nu_{\text{obs.}}$	$\Delta\nu^a$	$\nu_{\text{obs.}}$	$\Delta\nu^a$	$\nu_{\text{obs.}}$	$\Delta\nu^a$	$\nu_{\text{obs.}}$	$\Delta\nu^a$	$\nu_{\text{obs.}}$	$\Delta\nu^a$
$2_{02} \leftarrow 1_{01}$	12842.60	0.14								
$2_{11} \leftarrow 1_{10}$	13793.55	0.10								
$3_{13} \leftarrow 2_{12}$	18017.46	0.14								
$3_{03} \leftarrow 2_{02}$	19079.85	0.06								
$3_{22} \leftarrow 2_{21}$	19376.07	-0.12								
$3_{21} \leftarrow 2_{20}$	19672.65	-0.06								
$3_{12} \leftarrow 2_{11}$	20641.13	0.05					19471.15	0.16		
$4_{14} \leftarrow 3_{13}$	23944.61	0.12			23810.50	0.05	22811.82	0.10		
$4_{04} \leftarrow 3_{03}$	25115.78	-0.12			24975.23	0.20				
$4_{23} \leftarrow 3_{22}$	25776.24	-0.24	24943.20	-0.34	25619.12	-0.15				
$4_{22} \leftarrow 3_{21}$	26495.20	-0.10	25570.42	0.09						
$4_{13} \leftarrow 3_{12}$	29424.00	0.00					25886.41	0.13		
$5_{15} \leftarrow 4_{14}$	29815.41	0.13	28938.41	0.13	29650.41	0.01	28422.63	0.12	27192.42	0.13
$5_{05} \leftarrow 4_{04}$	30934.99	0.22	30049.98	0.10	30769.01	0.13	29501.71	-0.03	28219.01	0.05
$5_{24} \leftarrow 4_{23}$			31098.14	-0.20	31932.91	-0.08	30452.76	-0.34	28985.45	-0.23
$5_{23} \leftarrow 4_{22}$	33484.27	0.27			33258.04	0.05	31533.59	-0.02	29854.84	-0.05
$5_{14} \leftarrow 4_{13}$	34111.35	0.00	32975.22	0.21					30577.64	0.14

Table I. Continued

$J' \leftarrow J$	H_2CCCF_2		$\text{H}_2\text{C}^{13}\text{CCF}_2$		$\text{H}_2\text{C}^{13}\text{CCF}_2$		HDCCF_2		D_2CCCF_2	
	$\nu_{\text{obs.}}$	$\Delta\nu^a$	$\nu_{\text{obs.}}$	$\Delta\nu^a$	$\nu_{\text{obs.}}$	$\Delta\nu^a$	$\nu_{\text{obs.}}$	$\Delta\nu^a$	$\nu_{\text{obs.}}$	$\Delta\nu^a$
$6_{16} \leftarrow 5_{15}$	35627.78	0.12	34592.22	0.08	35433.04	-0.01	33984.96	-0.01	32531.12	0.04
$6_{06} \leftarrow 5_{05}$	36575.00	-0.52	35561.06	-0.10	36384.83	-0.14			33474.66	-0.11
$6_{25} \leftarrow 5_{24}$	38416.11	-0.51	37199.79	-0.23	38186.99	-0.19				
$6_{24} \leftarrow 5_{23}$									36127.62	0.01
$6_{15} \leftarrow 5_{14}$									36534.57	0.03

$^a \Delta\nu = \nu_{\text{obs.}} - \nu_{\text{calc.}}$ $\nu_{\text{calc.}}$ is obtained from the rotational constants given in Table II.

Table II. Rotational Constants (MHz) and Moments of Inertia ($\text{Amu} \cdot \text{\AA}^2$)^a of
1,1-Difluoroallene and its Carbon-13 and Deuterated
Isotopic Species in the Ground State.

	H_2CCCF_2	$\text{H}_2^{13}\text{CCCF}_2$	$\text{H}_2\text{C}^{13}\text{CCF}_2$	HDCCCF_2	D_2CCCF_2
A	10881.9±2.8	10879.3±4.5	10877.9±2.7	10695.1±5.7	10489.0±2.4
B	3667.34±0.03	3534.65±0.06	3642.16±0.05	3444.71±0.05	3251.49±0.01
C	2791.41±0.03	2713.90±0.05	2776.89±0.04	2671.91±0.04	2566.26±0.01
κ	-0.78347	-0.79887	-0.78604	-0.80732	-0.82702
I_a	46.442	46.453	46.459	47.253	48.182
I_b	137.805	142.978	138.758	146.711	155.429
I_c	181.047	186.218	181.994	189.145	196.931
Δ_c	3.200	3.213	3.223	4.820	6.680

^a Conversion factor: $505377 \text{ MHz} \cdot \text{Amu} \cdot \text{\AA}^2$

^b $\Delta_c = I_a + I_b - I_c$

Table III. Excited State Transitions (MHz) of 1,1-difluoroallene and its Deuterated Isotopic Species

	H_2CCCF_2				HDCCCF_2				D_2CCCF_2			
	$v(0,1)$		$v(1,0)$		$v(0,1)$		$v(1,0)$		$v(0,1)$		$v(1,0)$	
	$\nu(\text{obs.})$	$\Delta\nu$	$\nu(\text{obs.})$	$\Delta\nu$	$\nu(\text{obs.})$	$\Delta\nu$	$\nu(\text{obs.})$	$\Delta\nu$	$\nu(\text{obs.})$	$\Delta\nu$	$\nu(\text{obs.})$	$\Delta\nu$
$3_{03} \leftarrow 2_{02}$	1946.54	0.12	19134.99	=0.07	19541.35	0.23	19570.96	0.19				
$3_{12} \leftarrow 2_{11}$	20717.95	-0.09	20694.64	0.05	19541.35	0.23	19570.96	0.19				
$4_{14} \leftarrow 3_{13}$	23993.73	0.10	24012.32	0.09	22857.92	-0.09	22875.25	0.08				
$4_{04} \leftarrow 3_{03}$	25164.47	0.02	25193.05	-0.02								
$4_{23} \leftarrow 3_{22}$	25853.96	-0.27	25845.22	-0.34								
$4_{13} \leftarrow 3_{12}$	27521.71	0.13	27497.08	0.09	25796.40	0.15	25954.21	0.24				
$5_{05} \leftarrow 4_{04}$	30979.98	-0.12	31035.48	-0.08	29546.25	0.07	29595.95	0.05	28263.99	0.07	28305.53	0.04
$5_{15} \leftarrow 4_{14}$	29872.22	0.17	29901.23	0.07	28673.31	0.11	28503.12	0.11	27244.39	0.15	27266.01	0.14
$5_{14} \leftarrow 4_{13}$	34224.38	-0.02	54205.21	-0.02					30675.77	0.12	30657.47	0.13
$5_{24} \leftarrow 4_{23}$	32219.53	-0.35	32214.27	-0.43					29065.74	-0.23	29060.31	-0.26
$5_{23} \leftarrow 4_{22}$	33631.39	-0.09	33556.72	-0.01	31666.78	-0.02	31600.72	-0.06	29975.68	-0.04	29916.32	-0.03
$6_{16} \leftarrow 5_{15}$	35690.35	0.07	35732.09	0.04	34044.61	0.00	34082.96	0.03	32589.32	0.05	32620.75	0.07
$6_{06} \leftarrow 5_{05}$	36616.00	-0.38	36697.48	-0.34	34980.91	-0.14	35056.56	-0.15	33515.87	-0.15	33581.80	-0.13
$6_{24} \leftarrow 5_{23}$					38359.75	-0.04	38271.86	-0.03	36280.78	-0.02	36199.60	-0.02
$6_{15} \leftarrow 5_{14}$					38584.38	-0.07	38578.46	-0.10	36643.07	0.05	36633.78	0.07

Table IV. Rotational Constants (MHz) and Moments of Inertia ($\text{Amu} \cdot \text{\AA}^2$) of H_2CCF_2 , HDCCF_2 and D_2CCF_2 in Excited Vibrational States.

	H_2CCCF_2		HDCCCF_2		D_2CCCF_2	
	$v(0,1)$	$v(1,0)$	$v(0,1)$	$v(1,0)$	$v(0,1)$	$v(1,0)$
A	10758.36 ± 0.84	11017.02 ± 0.90	10557.08 ± 0.58	10845.42 ± 0.66	10337.86 ± 0.79	10654.86 ± 0.89
B	3683.68 ± 0.02	3676.42 ± 0.02	3459.53 ± 0.01	3453.13 ± 0.01	3265.03 ± 0.013	3259.27 ± 0.014
C	2795.19 ± 0.02	2799.40 ± 0.02	2675.52 ± 0.01	2679.41 ± 0.01	2569.83 ± 0.013	2573.09 ± 0.014
κ	-0.77685	-0.78655	-0.80105	-0.80941	-0.82101	-0.83019
I_a	46.9753	45.8724	47.8709	46.5982	48.8860	47.4316
I_b	137.194	137.464	146.083	146.353	154.785	155.058
I_c	180.802	180.531	188.889	188.615	196.658	196.409
Δ_c	3.366	2.806	5.064	4.336	7.013	6.081

^aConversion factor: $505377 \text{ MHz Amu} \cdot \text{\AA}^2$

Table V. Coordinates of Atoms (\AA) in the Principal Axis System of 1,1-difluoroallene (H_2CCCF_2).

	a	b	c
H_1	-2.8467	0.0	0.9262
H_2	-2.8467	0.0	-0.9262
C_2	-0.9795	0.0	0.0
C_3	-2.2853	0.0	0.0
C_1	0.3224	0.0	0.0
F_1	1.0803	1.0846	0.0
F_2	1.0803	-1.0846	0.0

Table VI. Structural Parameters for 1,1-Difluoroallene.

$r(C_2=C_3)$	1.306\AA
$r(C_1=C_2)$	1.302\AA
$r(C_3-H)$	1.086\AA
$r(C_1-F)$	1.323\AA
$\angle HC_3H$	117.8°
$\angle C_2C_3H$	121.1°
$\angle FC_1F$	110.2°
$\angle C_2C_1F$	124.9°

Table VII. Stark Coefficients and Dipole Moment of 1,1-Difluoroallene in the Ground State.

Transition	M	$\Delta\nu/E^2 \times 10^{-5} \left(\frac{\text{MHz}}{\text{V}^2/\text{cm}^2} \right)$		μ_a
		Observed	Calculated ^a	
$3_{03} \leftarrow 2_{02}$	0	-0.439	-0.430	2.09
	1	-0.121	-0.123	2.05
	2	-0.810	-0.798	2.08
$3_{12} \leftarrow 2_{11}$	1	-0.950	-0.931	2.09
	2	-3.214	-3.387	2.02
$3_{13} \leftarrow 2_{12}$	1	1.107	1.088	2.09

μ_a (average) = $2.07 \pm 0.03\text{D}$

$\mu_b = 0$ (by symmetry)

$\mu_c = 0$ (by symmetry)

^aCalculated from the average value.

VIBRATIONAL ANALYSES AND BARRIERS TO
INTERNAL ROTATION OF $\text{CH}_3\text{CCl}_2\text{F}$ and CH_3CHClF

ABSTRACT: The infrared spectra of gaseous and solid $\text{CH}_3\text{CCl}_2\text{F}$ and CH_3CHClF have been recorded from 140 to 4000 cm^{-1} . The corresponding Raman spectra of the liquids have also been recorded and depolarization values have been measured for the $\text{CH}_3\text{CCl}_2\text{F}$ molecule. Also the Raman spectrum of gaseous CH_3CHClF has been recorded. All spectra have been interpreted in detail and the 18 normal vibrations of both molecules have been characterized. The internal torsional mode for $\text{CH}_3\text{CCl}_2\text{F}$ was observed at 308 and 293 cm^{-1} in the spectra of the solid and gas, respectively. The threefold periodic barrier to internal rotation was calculated to be 6.08 kcal/mole for the solid and 5.57 kcal/mole for the gas. The internal torsional mode for CH_3CHClF was observed at 261 cm^{-1} in the spectra of the solid and the barrier was calculated to be 4.38 kcal/mole . The barriers are compared in a series of chloro, fluoro and bromo substituted ethane derivatives.

INTRODUCTION

In a continuing program of study of the torsional barriers in halogen substituted ethane derivatives, the barriers in $\text{CH}_3\text{CCl}_2\text{F}$ and CH_3CHClF were determined by direct observation of the torsional frequency in the far-infrared spectra. It is known that chlorine, and to a much lesser extent, fluorine, significantly effect the barrier to internal rotation about the C-C single bond^{1,2}. A large number of the torsional barrier studies in the past have been made by means of the microwave technique. However, due to the quadrupole splitting of chlorine, this technique does not readily lend itself to the study of the molecules in question.

No vibrational data have been previously reported for CH_3CHClF and only two references could be found in the literature concerning spectroscopic work on $\text{CH}_3\text{CCl}_2\text{F}$ ^{3,4}. Therefore, in order to confidently assign the torsional mode, we have undertaken the complete vibrational assignment of both molecules. Since torsional studies on molecules such as $\text{CH}_3\text{CF}_2\text{Cl}$, CH_3CCl_3 ¹ and CH_3CF_3 ¹ have recently been completed in this laboratory, the barriers for $\text{CH}_3\text{CCl}_2\text{F}$ and CH_3CHClF should provide interesting results for comparisons. The vibrational work reported by Smith et al.⁴ on $\text{CH}_3\text{CCl}_2\text{F}$ predicted the torsional frequency at 229 cm^{-1} based on the assignment of an overtone located at 459 cm^{-1} in the infrared spectrum. They calculated a barrier of 3.47 kcal/mole from this frequency. More recently a calculation was made by Abraham and Parry⁵ using steric and electrostatic interactions between non-bonded atoms, plus a torsional term to arrive at a barrier for $\text{CH}_3\text{CCl}_2\text{F}$ of 4.78 kcal/mole. It is the intention of our work to establish an accurate value for the barrier height of this molecule as well as that of CH_3CHClF in order to provide additional data for tests of such calculations.

EXPERIMENTAL

Both $\text{CH}_3\text{CCl}_2\text{F}$ and CH_3CHClF were obtained from the E. I. DuPont Company and were used without further purification, although their purity was checked by means of NMR and mass spectroscopy.

The far infrared spectra were recorded from 33 to 500 cm^{-1} with a Beckman Model IR-11 spectrophotometer. The atmospheric water vapor was removed from the instrument housing by flushing with dry air. The instrument was calibrated by using atmospheric water vapor⁶. Single beam energy checks were made periodically to insure the energy transmission was at least 10 - 15% at all times. A low temperature cell similar to one described earlier⁷ was employed to record the spectra of the solid samples. Modifications have been made to allow the circulation of cold nitrogen gas through a hollow brass cold finger. A wedged silicon window was used for the solid film support plate. Conventional vacuum deposition techniques were used to obtain the solid film on the silicon substrate with the additional precaution that the samples were allowed to sublime slowly onto the silicon plate from the solid phase. The silicon substrate was held at -190°C during deposition. The solid films were then annealed until there was no change in the spectrum. The spectrum of the gases were recorded in a variable-path cell equipped with polyethylene windows. Absorption paths up to 10 m were used with sample pressures up to 150 torr.

The Raman spectra were recorded on a Cary Model 82 Raman spectrophotometer⁸ equipped with an argon ion laser source with a frequency of 5145\AA for excitation. The spectrum of the gas sample was recorded using a multi-pass gas cell, and liquid samples were transferred to sealed capillary tubes.

The mid-infrared spectra were recorded from 4000 to 350 cm^{-1} with a

Perkin-Elmer Model 621 spectrophotometer. A low temperature cell equipped with a CsI window was employed to record the spectra of the solid samples. Again, conventional vacuum techniques were used to obtain the solid film on the CsI substrate. A 25 cm gas cell with CsI windows was employed to record the spectra of the gaseous samples.

VIBRATIONAL ASSIGNMENT

A. CH₃CCl₂F.

Assuming C_s symmetry, the 18 fundamental modes of 1,1,1-dichlorofluoroethane may be divided into 11a' and 7a" vibrations. The a' vibrations have polarized Raman bands and may have B, C or B/C hybrid contours in the infrared spectrum. The a" vibrations have depolarized Raman lines and type A band contours in the infrared spectrum.

The Raman spectrum of the liquid is shown in Fig. 1. The polarized lines were characterized by being quite narrow whereas the depolarized lines are usually quite broad with considerably weaker intensity. By using the Raman depolarization measurements along with the characteristic infrared band contours, a complete vibrational assignment is proposed. The frequencies for the observed bands along with the vibrational assignment is summarized in Table I.

The infrared spectrum of solid CH₃CCl₂F (Fig. 2A) shows a band at 3026 cm⁻¹. This band in the infrared spectrum of the gas (Fig. 2B) is obscured by the R branch of a type A band centered at 3012. The 3026 cm⁻¹ band has a Raman counterpart at approximately 3021 cm⁻¹ which is polarized; thus, we assign this band as the a' component of the antisymmetric CH₃ stretch, ν₁. As noted above, the infrared spectrum of the gaseous sample shows an A type band centered at 3012 cm⁻¹ with the corresponding Raman band depolarized. This

- 4 -

band is then unequivocally assigned as the a'' CH_3 antisymmetric stretching vibration, ν_{12} . The ν_2 symmetric a' CH_3 stretching vibration is assigned to the 2954 cm^{-1} C-type band in the mid-infrared spectrum of the gaseous sample. Its Raman counterpart occurs at 2949 cm^{-1} and is strongly polarized.

The a'' component of the antisymmetric CH_3 deformation, ν_{13} , is assigned to a Q branch in the infrared spectrum at 1442 cm^{-1} . This band has a somewhat distorted type A contour. In the Raman effect, a rather broad depolarized band is located at 1438 cm^{-1} . The ν_3 , antisymmetric CH_3 a' deformation, is thought to be degenerate with the 1438 cm^{-1} band even though the infrared spectrum of the low-temperature solid indicates a medium intensity peak at 1390 cm^{-1} . This is thought to be due to a combination of two fundamentals. The CH_3 symmetric deformation (a') is found as a polarized Raman line at 1383 cm^{-1} with a corresponding infrared type C band at 1385 cm^{-1} .

Between 1160 and 1050 cm^{-1} , there are three bands due to the in-plane and out-of-plane rocks and to the C-F stretching mode. Inspection of the infrared spectrum of the gas shows a band centered at 1159 cm^{-1} with a possible type C band contour. Its Raman counterpart occurs at 1156 cm^{-1} and is polarized. This band is, therefore, assigned to the ν_5 , CH_3 in-plane rock. The infrared spectrum of the solid shows a very strong band at 1106 cm^{-1} , with a highly polarized 1113 cm^{-1} Raman counterpart. One would expect the C-F stretch to be very strong in the infrared and highly polarized in the Raman, on this basis, the band is assigned to the ν_6 , CF stretch. The CH_3 out-of-plane rock, ν_{14} , is assigned to a band centered at 1092 cm^{-1} in the infrared spectrum of the gas. The type C band centered at 926 cm^{-1} with a polarized Raman counterpart is assigned as ν_7 , the C-C stretch. This 926 cm^{-1} band in the infrared spectrum appears to be of stronger intensity than expected for a C-C stretch. This enhancement of intensity is probably due to

the coupling of this mode with the CF stretching mode located at 1106 cm^{-1} .

The symmetric and antisymmetric CCl_2 stretches, ν_8 and ν_{15} , are assigned to bands at 591 and 750 cm^{-1} , respectively. Fig. 2 shows the 750 cm^{-1} band appearing mistakenly as a type B band; this is due to excess sample and a resultant bottoming off of the peak. With less pressure a type A band contour is quite evident. The 591 cm^{-1} band, however, gives rise to a type C band contour and a very strong polarized Raman line.

There are five other low lying vibrational modes expected for the CCl_2F entity; these are the CCF bend (a'), the CCl_2 rock (a''), the CCl_2 wag (a'), the CCl_2 twist (a'') and the CCl_2 scissors (a'). The ν_9 CCF mode occurs in the gas as a C-type band centered at 432 cm^{-1} , and as a strongly polarized Raman line at 433 cm^{-1} . The far infrared spectrum of the low temperature solid shows a weak band at 395 cm^{-1} . A depolarized band at 398 cm^{-1} in the Raman spectrum leads to the assignment of this band as the ν_{16} , CCl_2 rock. The CCl_2 wag, ν_{10} , and CCl_2 twist, ν_{18} , are assigned to bands at 380 and 296 cm^{-1} , respectively, based on the depolarization data. The polarized band at 260 cm^{-1} with a corresponding far infrared band at 264 cm^{-1} is assigned to ν_{11} , the CCl_2 scissors. Assignment of the torsional mode is deferred to a latter section.

B. CH_3CHClF

Since the CH_3CHClF molecule has no symmetry, the 18 fundamental modes all fall into the trivial "a" symmetry block. This introduces difficulty in assigning the vibrational modes since all of the bands should appear to be polarized in the Raman effect. In addition, having no plane of symmetry, we can no longer use band contours as an aid in the assignment. However, the infrared spectrum (Fig. 3b) of the gaseous sample does exhibit band contours, which is probably due to the dipole change accidentally being along a principal

axis.

Inspection of the infrared spectrum of the gas (Fig. 3b), indicates a band at 3015 cm^{-1} . A corresponding band in the Raman spectrum (Fig. 4b) of the gaseous sample is located at 3016 cm^{-1} . The infrared spectrum of the low-temperature solid (Fig. 3a) is not very informative in this spectral region, since all that is observed is a broad band centered at 3005 cm^{-1} , probably corresponding to the 3015 cm^{-1} band of the gas. Since this is the highest frequency band in the CH stretching region, we assign it to ν_1 , the "lone" CH stretch. The two CH_3 "antisymmetric" (in reference to the local C_{3v} symmetry) stretches occur at 2985 and 2974 cm^{-1} in the infrared spectrum of the gas. These two bands have Raman counterparts at 2987 and 2976 cm^{-1} , respectively.

A comparison of the Raman spectra of the liquid and gas phase (Fig. 4A & B) points out the higher definition in the spectrum of the gas, particularly in the C-H stretching region. Using only the spectrum of the liquid, the band at 2976 cm^{-1} would not have been observed due to the smearing out of the 2990 cm^{-1} band. The final CH_3 stretch gives a strong Raman line at 2945 cm^{-1} in the liquid phase and at 2952 cm^{-1} in the gas phase: The infrared spectrum of the gas indicates a band located at 2958 cm^{-1} and at 2941 cm^{-1} in the spectrum of the solid.

The region between 1500 and 1350 cm^{-1} should contain the three CH_3 deformations. The Raman spectra of the liquid and gas show very broad bands at 1450 and 1454 cm^{-1} , respectively. Comparison of similar molecules very often shows the deformations (degenerate for C_{3v} molecules) in this region to be accidentally degenerate. We feel that this also is the case with CH_3CHClF . The remaining CH_3 deformation, ν_7 , is readily assigned from the spectrum of the low temperature solid, where a band occurs at

1384 cm^{-1} . The 1407 cm^{-1} band can be attributed to a combination of two other fundamentals.

The CH bend, ν_8 , gives rise to an infrared band in the gas phase centered at 1284 cm^{-1} and a 1279 cm^{-1} band in the infrared spectrum of the solid. The CH bending mode, ν_9 , presents difficulty in making a proper assignment. In the spectrum of the liquid there is a broad shoulder at approximately 1135 cm^{-1} on the 1118 cm^{-1} band. A very strong band at 1138 cm^{-1} is indicated in the infrared spectrum of the gas. The Raman spectrum of the liquid has a band at 899 cm^{-1} , with a corresponding band at 917 cm^{-1} in the infrared spectrum of the solid. It is doubtful, however, that the CH bending mode would appear at such a low frequency, and thus we assign the CH bending mode, ν_9 , to the 1138 cm^{-1} band and the 899 cm^{-1} band as a combination mode.

The two CH_3 rocks, ν_{10} and ν_{12} , can be assigned to bands at 1118 cm^{-1} and 1020 cm^{-1} on the basis of the infrared spectrum of the low-temperature solid. The CF stretch, ν_{11} , is expected to be very strong in the infrared and can be confidently assigned to a 1081 cm^{-1} band in the infrared spectrum. The CC stretch, ν_{13} , is assigned to the 867 cm^{-1} band measured from the Raman spectrum of the liquid phase. The CCl stretch, ν_{14} , is easily identified by the Raman spectra of the liquid and gaseous phase at 681 and 693 cm^{-1} , respectively.

There are three other low-lying vibrational modes expected for the CClF group. These are ν_{15} , the CCF deformation, ν_{16} , the CCCl deformation, and ν_{17} , the C1F scissors. The CCF mode occurs in the Raman spectrum of the liquid at 481 cm^{-1} . The CCCl mode has a Raman line at 379 cm^{-1} , and the C1F scissors is found at 329 cm^{-1} . These vibrational modes are confidently assigned due to coincident low frequency bands observed in the far infrared spectrum of the solid.

TORSIONAL MODES AND BARRIERS

An inspection of Fig. 5 shows the far infrared spectrum of $\text{CH}_3\text{CCl}_2\text{F}$ of the low-temperature solid in the region of the CCl_2 twist and scissors. As additional sample is deposited onto the silicon plate, the growth of a band at 308 cm^{-1} is indicated. The far infrared spectrum of the gas was recorded and the torsional frequency was measured at 293 cm^{-1} . Since the spectrum was taken at such a low temperature, it is clear that this band is not a difference tone. Also it occurs at too high a frequency to be ascribed to a lattice mode. Thus, it is concluded that this band is the torsional mode since the five low frequency bending modes are confidently assigned to other bands and no other intramolecular fundamental is expected in this frequency range.

To calculate the torsional barrier, we have assumed a cosine type potential of the form:

$$V(\alpha) = \frac{1}{2} V_3(1 - \cos 3\alpha)$$

with all terms higher than threefold being considered negligible. The barrier was calculated according to the procedure outlined by Fateley and Miller,⁹ with the Tables of Hershbach¹⁰. The periodic barrier calculated using the solid phase frequency of 308 cm^{-1} was 6.08 kcal/mole. Using the gas phase frequency, the periodic barrier was calculated to be 5.57 kcal/mole.

In Fig. 6 is shown the far infrared spectrum of CH_3CHClF of the low temperature solid in the region between 140 and 350 cm^{-1} . As the sample was deposited on the silicon window, the band located at 261 cm^{-1} intensifies. Once again it can be reasoned that since the spectrum was taken at such a low temperature, it cannot be assigned to a difference band. Similarly it cannot be ascribed to a lattice mode or to a two phonon process because the band did not show the expected broadening or frequency shift with temperature that is observed for such modes. Since the three low frequency bending modes,

are confidently assigned to other bands, it is concluded that this 261 cm^{-1} band corresponds to the torsional frequency. Using this frequency to calculate the period barrier we arrive at a value of 4.38 kcal/mole.

DISCUSSION

In Table III are listed the barrier heights for a series of halogen substituted ethane molecules. This series of molecules can be arranged in a number of ways in order to see the effect of adding bromine, chlorine and fluorine, separately and in combination, to "one end" of the ethane molecule. The variation of the barriers for this is depicted in Fig. 7. As expected initial substitution of the ethane molecule resulting in either $\text{CH}_3\text{CH}_2\text{Cl}$ or $\text{CH}_3\text{CH}_2\text{F}$ produces an increase in the barrier. If non-bonded interactions are the main cause of rotational hindrance about the C-C single bond, then it follows that replacement of a hydrogen by an atom of larger size would cause an increase in the barrier to methyl rotation. Since chlorine is more massive than fluorine it is also expected that chlorine should have a greater effect on the barrier than will the fluorine atom. In fact, as Fig. 7 shows, the barriers are in the order $\text{CH}_3\text{CH}_2\text{Br} > \text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{CH}_2\text{F}$. Unfortunately on progressing to CH_3CHClF we run into our first contradiction. Although replacement of a second hydrogen in $\text{CH}_3\text{CH}_2\text{F}$ by a chlorine atom results in a barrier increase, the similar process of going from $\text{CH}_3\text{CH}_2\text{Cl}$ to CH_3CHClF produces a barrier decrease. Progression from CH_3CHClF to either $\text{CH}_3\text{CF}_2\text{Cl}$ or $\text{CH}_3\text{CCl}_2\text{F}$ does fall in line with theory. That is, the molecule with two chlorine atoms in combination with a fluorine atom yields a higher barrier than the molecule with two fluorine atoms and a chlorine atom. On going from $\text{CH}_3\text{CF}_2\text{Cl}$ to CH_3CF_3 a lowering of the barrier is expected, since we are replacing a chlorine by a fluorine, and this is the case. Introduction of a second anomaly, however, is graphically

depicted in going from $\text{CH}_3\text{CCl}_2\text{F}$ to CH_3CCl_3 . Replacement of a fluorine atom by a chlorine atom should markedly increase the barrier. However, using solid phase values, the barrier decreases by 600 calories, and by 570 calories using gas phase values. Finally a comparison can be made of the vertical series of haloforms where the barrier increases in the order $\text{CH}_3\text{CBr}_3 > \text{CH}_3\text{CCl}_3 \geq \text{CH}_3\text{CF}_3$.

Certainly, in conclusion, we can say that the non-bonded interactions play an important, if not major, role in determining the barrier to internal rotation. However, it is also obvious that other factors are important, especially among the interhalogen substituted ethane molecules, and that these factors can at times cause a reversal of the order predicted strictly by steric effect considerations. The forces could include such phenomena as halogen-halogen interaction, hydrogen-halogen (especially fluorine) interaction, and symmetry considerations.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support given this work by the National Aeronautics and Space Administration by Grant number NGL-41-002-003.

REFERENCES

1. J. R. Durig, S. M. Craven, K. K. Lau, and J. Bragin, J. Chem. Phys. 54, 479-487, (1970).
2. J. R. Durig, A. E. Sloan and J. D. Witt, J. Phys. Chem., 78, 000 (1973).
3. J. R. Durig, S. M. Craven and C. W. Hawley, and J. Bragin, J. Chem. Phys., 57, 131 (1972).
4. D. C. Smith, G. M. Brown, J. R. Nielson, R. M. Smith and C. Y. Liang, J. Chem. Phys. 20, 473 (1952).
5. R. J. Abraham and K. Parry, J. Chem. Soc. B (1970) 3, 539-45.
6. R. T. Hall and J. M. Dowling, J. Chem. Phys., 47, 2454 (1967).
7. F. G. Baglin, S. F. Bush, and J. R. Durig, J. Chem. Phys. 47, 2104 (1967).
8. This instrument was purchased with funds from the National Science Foundation through Grant No. GP-28068.
9. W. G. Fateley and F. A. Miller, Spect. Acta, 17, 857 (1961).
10. D. R. Herschbach, J. Chem. Phys. 31, 91 (1959).

Table I. Observed Vibrational Frequencies for 1,1,1-dichlorofluoroethane.

Raman $\Delta\nu(\text{cm}^{-1})$	Infrared $\nu(\text{cm}^{-1})$		Description
Liquid	Gas	Solid	
~ 3021 (sh) p	~ 3028	3026	$\nu_1(a')$ CH_3 antisymmetric stretch
3012 m,dp	3012 w,A	3007	$\nu_{12}(a'')$ CH_3 antisymmetric stretch
2984 sh,vw		2981	$\nu_{15} + \nu_{13} + \nu_9 = 2989$
2949 s,p	2954 w,C	2947	$\nu_2(a')$ CH_3 symmetric stretch
2896 vvw	-	-	?
2863 m,p	-	2850	$2\nu_{13} = 2862$
-	-	2812	$\nu_{13} + \nu_4 = 2812$
2750 m,p	-	2748	$2\nu_4 = 2762$
1438 m,dp	1442 w,A?	1431	$\nu_{13}(a'')$ CH_3 antisymmetric deformation
-	-	1390	$\nu_{18} + \nu_6 = 1398$
-	1442 w,A?	1431	$\nu_{3,13}(a',a'')$ CH_3 antisymmetric deformation
1383 w,p	1385 m,C	1381	$\nu_4(a')$ CH_3 symmetric deformation
-	-	1263 vw	$\nu_7 + \nu_{10} = 1287$
-	-	1249 vw	?
-	-	1226 w	?
-	-	1207 w	$\nu_7 + \nu_{17} = 1217$
-	1191 (sh)	1169	$2\nu_8 = 1182$
1156 p	1159 s,A?	1146	$\nu_5(a')$ CH_3 rock
-	-	1124	$\nu_{15} + \nu_{16} = 1126$
1113 p	1119 s	1106	$\nu_6(a')$ CF stretch
1089 dp	1092 vs,?	1077	$\nu_{14}(a'')$ CH_3 wag
-	-	1042	$\nu_{15} + \nu_9 = 1065$

Table I. Continued

Raman $\Delta\nu(\text{cm}^{-1})$	Infrared $\nu(\text{cm}^{-1})$		Description
Liquid	Gas	Solid	
-	-	1016	$\nu_{15} + \nu_{18} = 1023$
-	966 vw	953 m	$\nu_8 + \nu_{10} = 969$
920 p	926 s, C	909	ν_7 (a') CC stretch
-	-	889 m	$\nu_8 + \nu_{17} = 899$
795	-	772	$2\nu_{16} = 790$
745 dp	750 vs, A	731	ν_{15} (a'') CCl_2 antisymmetric stretch
680 p	681 w, C	673	$\nu_{16} + \nu_{18} = 687$
591 p	591 s	591	ν_8 (a') CCl_2 symmetric stretch
545 vw	-	543	$\nu_8 + \nu_{11} = 554$
433 p	432 m, C	434	ν_9 (a') CCF in-plane bend
398 dp	-	~395	ν_{16} (a'') CCF out-of-plane bend
380 p	380 vw	378	ν_{10} (a') CCl_2 wag
296 dp	301	292	ν_{18} (a'') CCl_2 twist
260 p	262	264	ν_{11} (a') CCl_2 scissor
-	293	308	ν_{17} (a'') CH_3 torsion

Table II. Observed Vibrational Frequencies for 1,1-Chlorofluoroethane.

Gas	Raman $\Delta\nu(\text{cm}^{-1})$	Liquid	Gas	Infrared $\nu(\text{cm}^{-1})$	Solid	Description
3016 vs		3012	3015 m		3005 bd	ν_1 CH stretching
3003 w		-	3001 vw		-	
2987 s		2990 bd	2985 vw		-	ν_2 CH ₃ antisymmetric stretch
2976 s		-	2974 m		-	ν_3 CH ₃ antisymmetric stretch
2952 vs		2945	2958 vw		2941	ν_4 CH ₃ symmetric stretch
2886 w		-	-		-	
2894 vv		-	2896 vv		-	$2\nu_5 = 2908$
2879 w		2875	2865 vw		2860	$\nu_5 + \nu_6 = 2872$
2810 vw		2805	-		-	$\nu_5 + \nu_7 = 2826$
2760 vw		2758	-		2759	$2\nu_7 = 2768$
2692 vv		-	-		-	?
1614 vw		1607	-		-	
1454 b		1450 + 1448	too broad		1436	ν_5 CH ₃ deformation
1454 b		1450 + 1448	too broad		1436	ν_6 CH ₃ deformation
-		-	1411 m		1407	$\nu_{11} + \nu_{17} = 1411$
-		1370 vw	1394 m		1384	ν_7 CH ₃ deformation
1287 w		1282	1284 s		1279	ν_8 CCH bend
-		1135	1138 s		1136	ν_9 CCH bend
1123 w		1118	1124 s		1118	ν_{10} CH ₃ rock
1112 w		-	1113		1081	ν_{11} CF stretch
1027 w		1020	1026 m		1020	ν_{12} CH ₃ wag
899 w		899	930 m		917	$\nu_{14} + \nu_{18} = 931$

Table II. Continued

Raman $\Delta\nu(\text{cm}^{-1})$		Infrared $\nu(\text{cm}^{-1})$		Description
Gas	Liquid	Gas	Solid	
867 m	867	897 m	881	ν_{13} C-C stretch
693 s	681	692 s	670	ν_{14} CCl stretch
570 vvw	570 w	570 m	567	?
	548			
479 m	481	481 w	478	ν_{15} CCF deformation
379 m	379	379 w	379	ν_{16} CCl deformation
327 w	329	-	330	ν_{17} C1F scissor
-	-	-	261	ν_{18} CH ₃ torsion

Table III. Torsional Barriers for Some Chloro-, Fluoro- and Bromo Ethanes.

Molecule	Gas	Solid	Reference
CH_3CH_3	2.928	3.24	a,b
$\text{CH}_3\text{CH}_2\text{Br}$	3.68	4.53	c,d
$\text{CH}_3\text{CH}_2\text{Cl}$	3.71	4.48	e,f
$\text{CH}_3\text{CH}_2\text{F}$	3.3	-	g
CH_3CHClF	-	4.38	h
$\text{CH}_3\text{CF}_2\text{Cl}$	4.40	4.77	i
$\text{CH}_3\text{CCl}_2\text{F}$	5.57	6.09	h
CH_3CF_3	3.1	3.29	j
CH_3CCl_3	5.0	5.49	j
CH_3CBr_3	5.5	6.0	k,i

^aR. R. Getty and G. E. Leroi, 24th Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, September, 1969 Paper Q-7

^bS. Weiss and G. E. Leroi, J. Chem. Phys. 48, 962 (1968).

^cJ. R. Durig, C. M. Player, Jr., and J. Bragin, J. Chem. Phys., 54, 460, (1971).

^dC. Flanagan and L. Pierce, J. Chem. Phys. 38, 2963 (1963).

^eC. M. Player, private communication.

^fR. H. Schwendeman and G. D. Jacobs, J. Chem. Phys. 36, 1245 (1962); W. G. Fately and F. A. Miller, Spect. Acta, 19, 611 (1963).

^gG. Sage and W. Klemperer, J. Chem. Phys. 39, 371 (1963).

^hThis Work.

ⁱJ. R. Durig, S. M. Craven, C. W. Hawley and J. Bragin, J. Chem. Phys. 57, 131 (1972).

^jJ. R. Durig, S. M. Craven, K. K. Lau and J. Bragin, J. Chem. Phys., 54, 479-877 (1971).

^kH. W. Thompson and R. B. Temple, J. Chem. Soc., 903, 1428 (1948).

FIGURE CAPTIONS

Figure 1. Raman spectrum of liquid $\text{CH}_3\text{CCl}_2\text{F}$.

Figure 2. A. Infrared spectrum of solid $\text{CH}_3\text{CCl}_2\text{F}$. B. Infrared spectrum of gaseous $\text{CH}_3\text{CCl}_2\text{F}$.

Figure 3. A. Infrared spectrum of solid CH_3CHClF . B. Infrared spectrum of gaseous CH_3CHClF .

Figure 4. A. Raman spectrum of liquid CH_3CHClF . B. Raman spectrum of gaseous CH_3CHClF .

Figure 5. Far infrared spectrum of solid $\text{CH}_3\text{CCl}_2\text{F}$.

Figure 6. Far infrared spectrum of solid CH_3CHClF .

Figure 7. Barriers to methyl rotation in a series of chloro, fluoro, and bromo ethanes.

